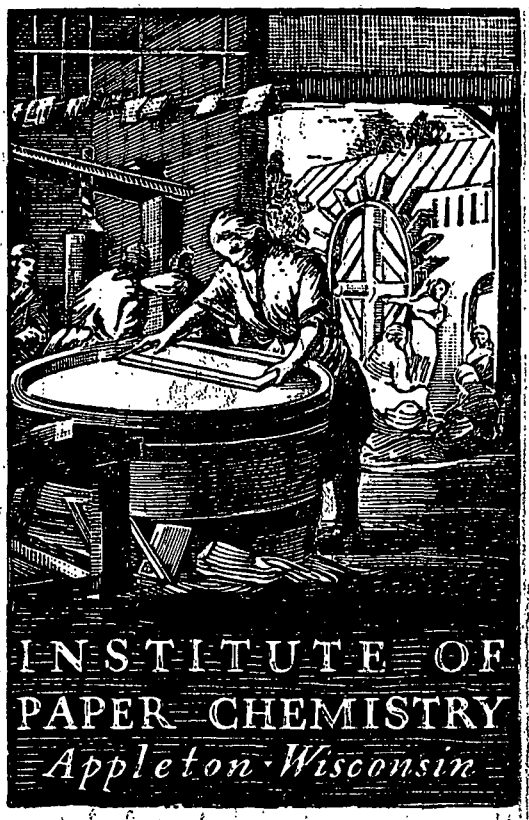

AUTOMATIC INSTRUMENTATION FOR CHEMICAL ANALYSIS OF PULP

Project 2634

Report Four

A Progress Report

to

MEMBERS OF GROUP PROJECT 2634

August 22, 1969

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

AUTOMATIC INSTRUMENTATION FOR CHEMICAL ANALYSIS OF PULP

SUMMARY

In a search for a procedurally simplified method for routine determination of lignin in pulp, the reaction of pulp with nitric acid was investigated extensively. It was discovered that an acid-soluble yellow substance extracted from the pulp upon reaction with hot nitric acid had an extinction maximum, or shoulder, at 425 nm., and that the intensity at this wavelength is a simple direct function of the lignin content of the pulp. The results of correlation analysis of the data show that the Nu-Number is an accurate (± 2%) linear function of both Klason lignin and Kappa number for softwood unbleached kraft pulps below about 70% yield. With more limited data available, the same appears to be true of softwood unbleached sulfite pulp. The method applied to hardwoods seems to indicate a different relationship for lignin content of each species of wood. This is not true of softwoods, however. Like the Kappa number, the linear relationship between lignin content and Nu-Number seems to break down at yield levels above 70%. Applied to high-yield hardwood neutral sulfite pulp, no useful relationship was found between Klason lignin and Nu-Number. However, for the two species pulped, a simple linear relationship existed between yield and Nu-Number. The procedure finally adopted calls for reaction of 0.25 g. of pulp with 200 ml. of 14% (w/v) HNO_3 for 8-10 minutes at 85°C., followed by cooling, filtering, and measuring the light absorbance of the liquid phase at 425 nm. The Nu-Number is calculated from the actual sample weight, the absorbance value, and the equivalent absorbance of a standard potassium dichromate solution.

In a similar search for a rapid, nongravimetric means of measuring the mass of dry fiber in a sample of pulp slurry, an investigation was made of the

relationship between the thickness of a confined, compressed pad of fibers under water-saturated conditions and the actual ovendry weight of such a pad. It was found that under static load and at temperatures up to 85°C., the o.d. weight of the pad after two minutes of compression was a single, direct function of its thickness, with an overall measurement accuracy of about 2%. The procedure thus established formed the design basis of an automatic device which was built and tested extensively in the laboratory.

Combining the principles of the Nu-Number test and the pulp sample measurement procedure with the mechanical design of the automated sample-measuring device has resulted in a completely automatic system for the on-line measurement o residual lignin in pulp. The system has been extensively tested in the laborator using various unbleached softwood kraft pulps. It appears that the results of th automatic measurements are generally within a relative deviation range of 3-5%. Although completely automatic, the system is not continuous, but makes repetitive batch tests at the rate of one test every 17 minutes.

Future work is proposed that involves packaging the system in a manner suitable for an industrial environment, constructing and laboratory testing of an already designed raw stock sampler, and, finally, installation of the entire syste in a mill for an industrial trial. The cost of this future work is estimated at $60,000 for a time period of 6-8 months.

INTRODUCTION

Project 2634 was established August 1, 1966, with two specific and interrelated objectives:

1. To develop a method for the quantitative, automatic sampling of pulp slurries, and

2. To develop a method for automatic determination of residual lignin in pulp.

The project has been supported financially by twenty-two companies at a total budget of $166,000. That the objectives have been reached is outlined in this report, a portion of which is a condensation of information contained in the three previous reports.

While the objectives have been reached, a logical conclusion to the work seems to be to finalize the design of the entire instrumental system to the point where it can be turned over under license to a reputable concern for manufacture and marketing. Before this can be done, it is essential that the system, until now used only in the laboratory, be packaged in a manner suitable for a pulp mill environment and then actually installed in a pulp mill, placed on-stream, and tested for several months. The data obtained from such a mill trial will be invaluable in establishing the design of final "production" units.

It is, of course, in these final "production" units that the ultimate value of the development work carried out under this project will be found, because the pulping industry will for the first time have available a reliable means of automatically monitoring its product for a major processing variable – residual lignin.

Accordingly, the final phase of this project is described in this report under the Future Work chapter, and time and budget estimates are set forth.

THE NU-NUMBER, A MEASURE OF LIGNIN IN PULP

REVIEW OF METHODS

Kurschner (1) presented a clear and thorough discussion of some of the basic problems in quantitative measurement of lignin, and favors a method whereby the lignin is nitrated and measured gravimetrically as nitrolignin. Seidel (2) measured the amounts of gases formed during reaction of lignin with nitric acid, and used their sum as a measure of the lignin. Richter (3) used the intensity of the soluble yellow-colored reaction product with nitric acid as an index of the amount of lignin. Bartunek (4) modified Seidel's method and applied it to the determination of lignin in high-purity pulps by measuring the color intensity in the ultraviolet region.

Nakajima and Hachihama (5) discovered that aqueous o-phenolsulfonic acid dissolves lignin and that the lignin could be determined as the difference in U.V. spectra of the reagent present and the soluble product.

The method of gravimetric measurement of lignin after hydrolysis in mineral acids is widely practiced and has been subjected to numerous studies and modifications. Roudier's (6) study showed large differences in the results obtained from various modifications of this method, as did that of a similar study by Polcin and Samkova (7). Jayme and Rapp (8) have proposed a two-acid procedure, which was included in Roudier's and in Polcin and Samkova's studies.

Measurement of the absorbance of ultraviolet radiation at 280 *nm.* after dissolution of pulp or wood in various solvents has been proposed as a way of quantitative lignin measurement. Sjostrom and Enstrom (9) investigated the solvent cadoxen, while Johnson, *et al.* (10) and Marton (11) looked into the use of acetyl bromide.

Marton and Sparks (12) developed a method of measuring lignin in pulp and paper by multiple internal reflectance in the infrared, which was calibrated against their acetyl bromide technique.

Perhaps the most widely used procedure for measuring lignin in pulp is that involving its oxidation by aqueous potassium permanganate, possibly because of its widespread application in pulping and bleaching control. Historically, this technique has been referred to as the "K" number procedure, best exemplified by the standard TAPPI method (13). Tasman and Berzins (14-18) shed considerable light upon the use of potassium permanganate for this purpose, and their efforts have resulted in a modified procedure called the Kappa number procedure, since adopted as a standard TAPPI method (19).

From the standpoint of application as a control technique in a pulp mill, the various gravimetric and spectrophotometric procedures discussed so far, with the possible exception of Marton and Sparks's multiple internal reflectance method, have obvious handicaps involving either procedural complexity or excessive time requirements. The titrimetric methods involving potassium permanganate do not suffer as severely from these drawbacks, especially in view of the development of the "5-minute" Kappa number test (18). However, the permanganate methods still require the use of two accurately standardized volumetric solutions plus several other reagents, and the conditions under which the test must be performed are rather stringent, as are the calculation and correction of results. Nevertheless, the Kappa number procedure is eminently suitable as a standard reference method and is almost universally accepted as such.

In the interest of possibly finding a more simple, but acceptably accurate procedure for routine measurement of residual lignin in pulp for application in mill process control, an extensive and intensive review of past work in this field was

undertaken, a brief summary of which is presented here. Continued study of lignin determination methods, along with an analysis of concurrent laboratory work, led to the work reported in this paper: an investigation of the possibility of measuring pulp lignin content by reaction with nitric acid as an extension of the work of Seidel and of Bartunek.

EXPERIMENTAL: KRAFT PULPS

Development of Procedure

Bartunek reacted 15 g. of high-purity pulp with 13% (w/v) HNO_3 at 40°C. for 45 minutes, filtered off the pulp, and recorded the light absorbance spectrum. He found two maxima, one at 261 nm. and another that varied between 330 and 338. He also measured the absorbance at 420, but did not show the spectrum in this region. The results were calculated as "lignin number" against the absorbance of a standard potassium dichromate solution.

The possible use of an absorbance shoulder or maximum in the visible region near 420 nm. appeared attractive for practical reasons. A few preliminary experiments showed that Bartunek's 45-minute reaction time could be cut down to about 20 minutes by raising the temperature to 70°C. Figure 1 shows three absorbance spectra in the region 350-500 nm. measured on a Beckman DB spectrophotometer with recording and automatic scanning functions. Matched 1.0-cm. silica cells were used. The spectra from the two pulps were made on the filtrate derived from reacting 30 mg. of ground (40-mesh) pulp with 50 ml. of 14% (w/v) HNO_3 for 20 minutes at 70°C., and were measured against the 14% HNO_3 reagent. The 14% HNO_3 spectrum was measured against distilled water. Figure 2 shows a similar spectrum of 100 mg./l. of potassium dichromate in distilled water (pH 5.1), while Fig. 3 illustrates that $K_2Cr_2O_7$ measured at 425 nm. follows Beer's Law.

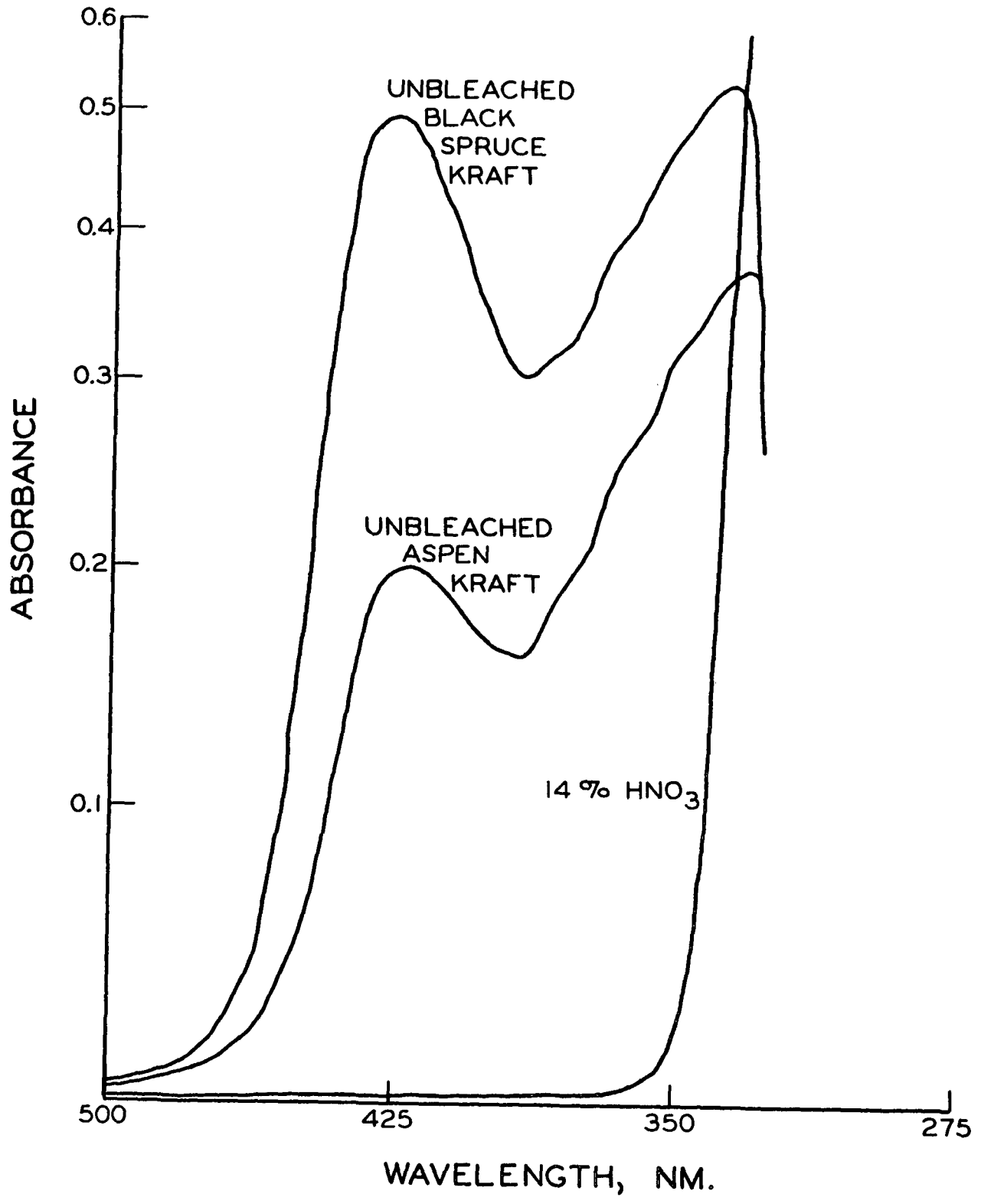


Figure 1. Absorbance Spectra of the Reaction Product with Nitric Acid of Kraft Pulps and of Nitric Acid of Itself

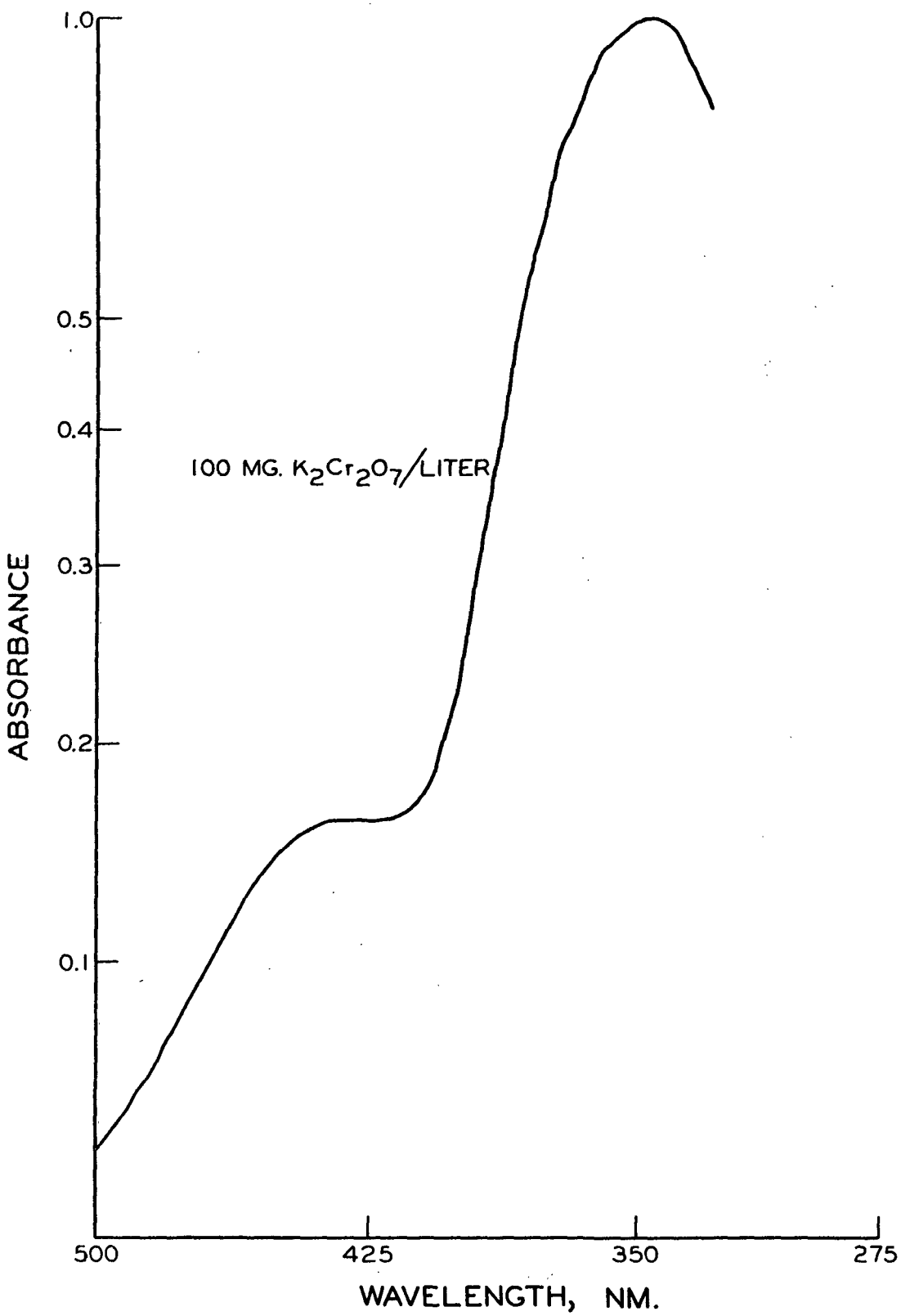


Figure 2. Absorbance Spectrum of Potassium Dichromate

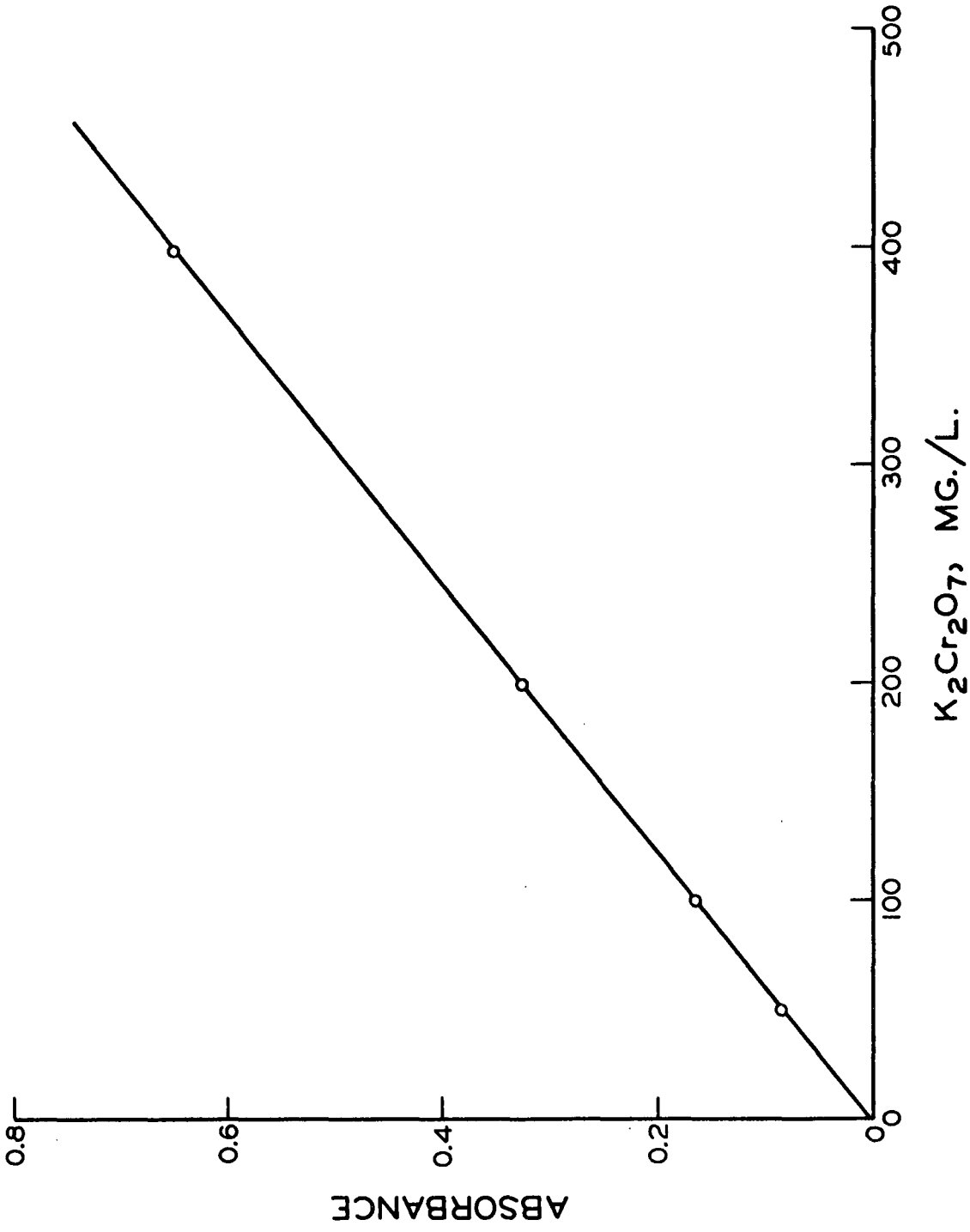


Figure 3. Reference Curve of Potassium Dichromate Standards at 425 nm.

Figures 1-3 show that the yellow color extracted from pulp containing lignin by reaction with 14% nitric acid has an absorbance maximum at 425 nm. and that by virtue of its obedience of Beer's Law at 425 nm., $K_2Cr_2O_7$ is a suitable reference material.

Additional experiments wherein the reaction time and temperature were varied showed that increasing temperature shortened the reaction time, but that the absorbance at 425 nm. passed through a maximum that increased in sharpness at higher temperatures. The results are shown in Fig. 4 and 5.

Establishment of Lignin - Nu-Number Relationship

To define the relationship between pulp lignin content and the intensity of the yellow color at 425 nm., pulp samples were obtained from two general sources: (1) laboratory cooks and (2) pulp mills. In the laboratory, wood was cooked in a seven-unit digester to provide a wide range of yield under constant cooking conditions. Commercial pulps were obtained from seven different mills representing both batch and continuous processes and a variety of wood species. Table I gives the conditions for the laboratory cooks in the multiunit digester. Table II lists the available data concerning cooking conditions for the commercial pulps. Many samples of commercial pulps were obtained to represent about 24 hours' production, and thus obtain a representative picture of K-number fluctuations in each mill.

At this time, also, a fixed procedure was adopted for the nitric acid reaction, and the name "Nu-Number" was chosen to identify the procedure and the results. The procedure was as follows:

Thirty milligrams (± 5 mg.) of dry, ground (40-mesh) pulp were weighed exactly into a 100-ml. beaker. Fifty ml. of 14% (w/v) HNO_3 were added and the beaker was placed in a 70°C. water bath for a period of time determined by the rate

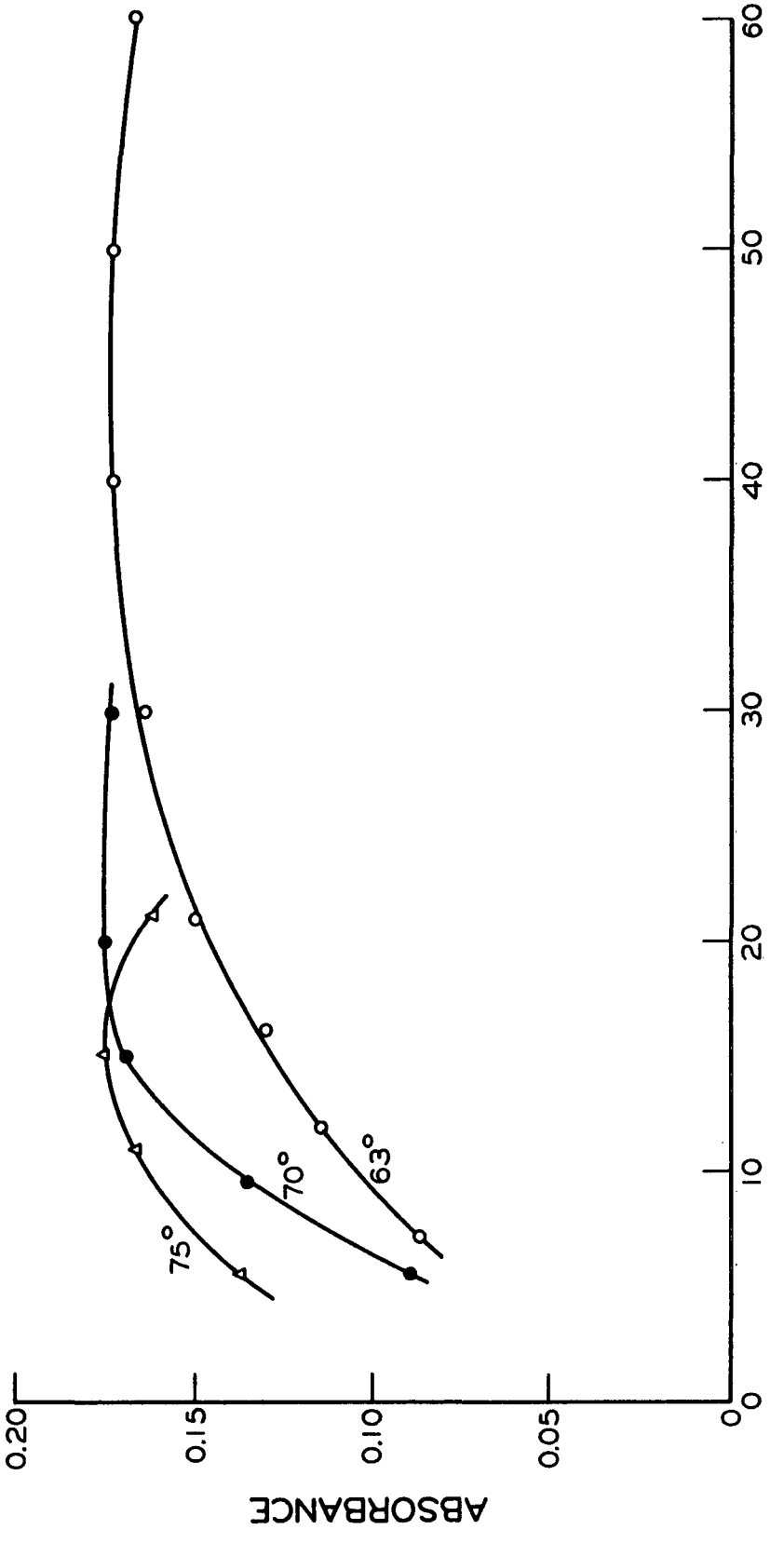


Figure 4. Absorbance of Unbleached Aspen Kraft Pulp Extract at 425 nm. as a Function of Time and Temperature

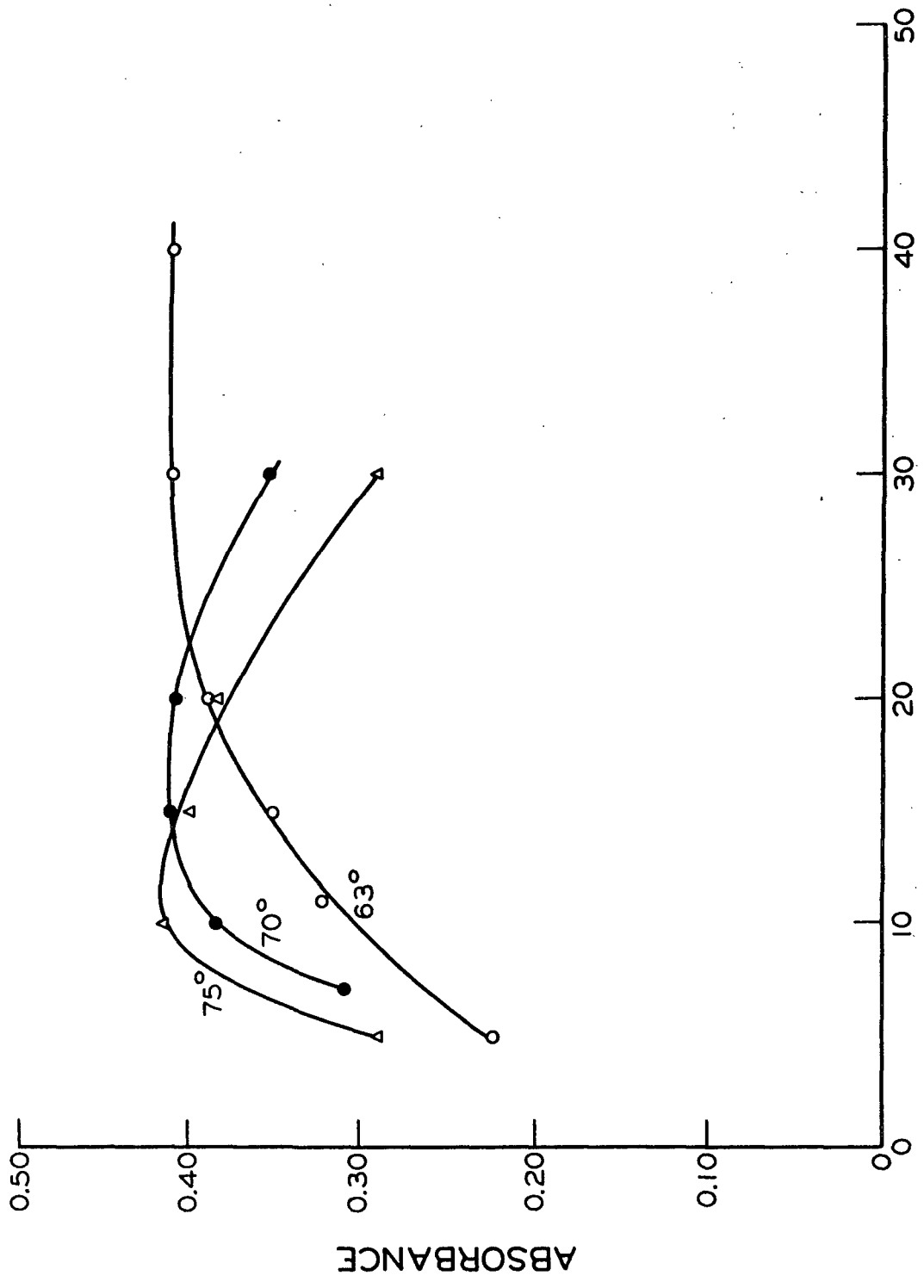


Figure 5. Absorbance of Unbleached Loblolly Pine Kraft Pulp at 425 mm. as a Function of Time and Temperature

TABLE I

CONDITIONS OF MULTIUNIT DIGESTER COOKS

Cook No.	Wood Species	White Liquor Composition		Liquor-to-Wood Ratio	Digester Temp., °C.	Cooking Times, min.
		Sulfidity, %	Effective Alkali, g./l. as Na_2O			
I	Loblolly pine	40	40	6:1	140	5, 15, 35, 75, 130, 190, 320
II	Loblolly pine	20	20	6:1	160	5, 15, 35, 75, 130, 190, 320
III	Aspen	33	29	10:1	165	15, 20, 25, 30, 35, 45, 80
IV	Aspen	33	52	10:1	165	15, 20, 25, 30, 35, 45 80
V	Aspen	33	29	10:1	140	15, 40, 80, 130, 190, 250, 320
VI	Aspen	33	29	10:1	140	40, 50, 60, 70, 80, 90, 110
VII	Aspen	25	14	6:1	170	20, 25, 40, 50, 60, 70, 90, 110, 140
VIII	Black spruce	25	18	6:1	170	20, 40, 60, 70, 80, 100, 110
IX	Southern pine	25	18	6:1	170	25, 40, 60, 70, 80, 100, 110
X	Douglas-fir	25	18	6:1	170	25, 40, 60, 70, 80, 100, 110

TABLE II

COOKING DATA FOR COMMERCIAL PULP SAMPLES

Mill	Wood Species	Max. Temp., °F.	White Liquor Composition: Effective Alkali, lb./ft.^{3} as Na_2O	White Liquor Composition: Sulfidity, %	Total Liquor-to-Wood Ratio
1	Mixed lodgepole, ponderosa, and jack pine	360	5.8	36	ND
2	Douglas-fir	355	5.7	24	3:1
3	Douglas-fir + some pine	348	5.3	25	3.5:1
4	Loblolly, slash, and longleaf pine mixture	343	4.9	25	ND
5	Mixed pines	337	6.0	25	ND
6	Mix of Douglas-fir, west. hemlock, pine, spruce, and larch	340	4.2	23	ND
7	Southern pines	310	5.7	27	3.4

ND = not determined.

of color development for that particular pulp (see below). The beaker contents were then filtered through Whatman no. 40 filter paper into a low-actinic glass test tube, the tube was cooled for about a minute under running tap water to about 30°C., and the absorbance of the filtrate was measured at 425 nm. against 14% HNO_3 in 1.0-cm. pyrex cells on a Beckman DB spectrophotometer. Using a reference curve of $K_2Cr_2O_7$ similar to that in Fig. 3, the equivalent milligrams of $K_2Cr_2O_7$ were obtained from the absorbance of the filtrate and the Nu-Number was calculated from Equation (1),

$$Nu = \frac{30M}{W} \qquad (1)$$

where:

$\underline{M}$ = mg. of $K_2Cr_2O_7$ and

$\underline{W}$ = mg. of pulp sample.

The exact heating time was predetermined for each wood species used in the laboratory cooks and each set of commercial pulps by measuring the time at which the maximum Nu-Number was obtained, as illustrated in Fig. 6 and 7. Thus, for the laboratory pulps, the reaction time was 20 minutes, while for the commercial pulps, it varied between 20 and 30 minutes.

All of the pulp samples were analyzed for Klason lignin, Kappa number, and Nu-Number. In addition, the yield of the laboratory cooks was measured. Neither Kappa number nor Nu-Number was measured for pulp above about 70% yield. The data for the laboratory pulps are shown in Table III and for the commercial pulps in Table IV.

According to Tasman (17), a linear relationship exists between Kappa number and Klason lignin for pulps below 70% yield, and this relationship is expressed by Equation (2).

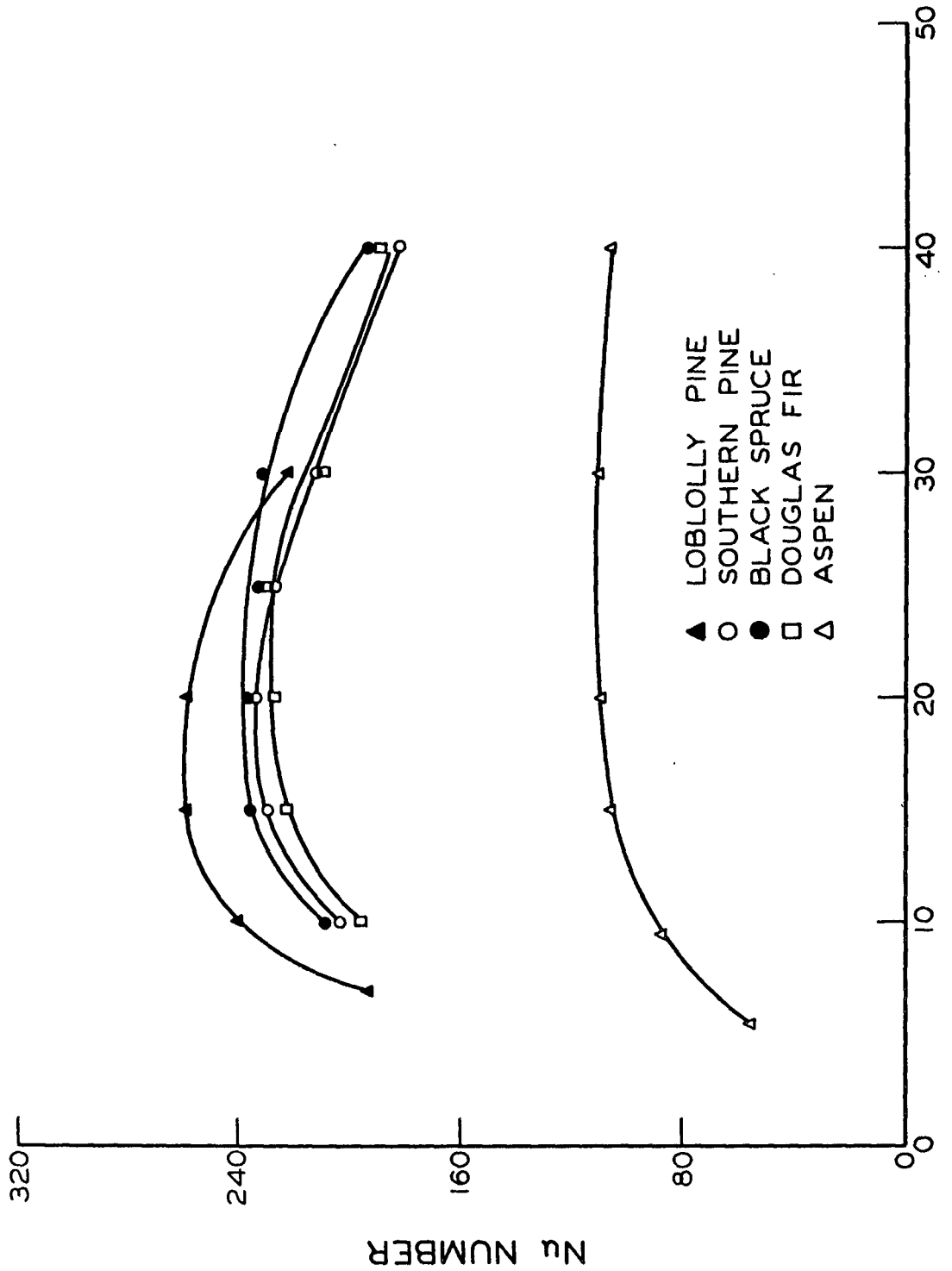


Figure 6. Reaction Rate Curves of Experimental Pulps with 14% HNO_3 at 70°C.

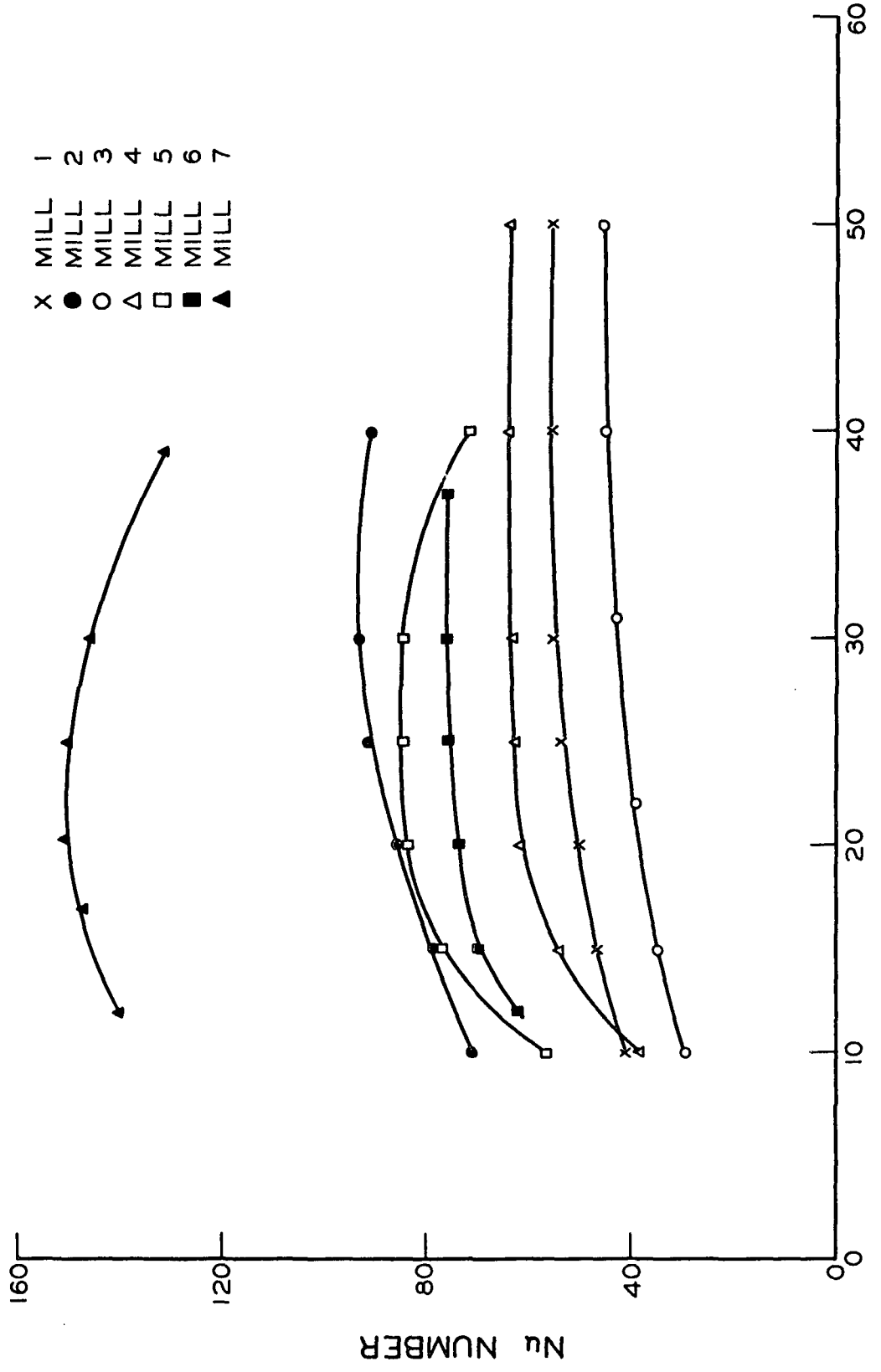


Figure 7. Reaction Rate Curves of Commercial Pulps with 14% HNO_3 at 70°C.

TABLE III

ANALYSIS OF LABORATORY PULPS

Cook	Cooking Time, min.	Yield, %	Nu-Number	Klason Lignin, %	Kappa Number
I	5	97.6	ND	29.3	ND
	15	82.1	ND	29.2	ND
	35	77.8	ND	27.6	ND
	75	72.4	ND	25.9	ND
	130	68.2	325	23.3	140
	190	63.3	282	19.4	128
	320	53.8	219	13.7	101
II	5	90.0	ND	30.5	ND
	15	80.1	ND	29.7	ND
	35	71.0	ND	27.0	ND
	75	66.0	334	22.9	146
	130	58.0	259	17.2	119
	190	53.8	205	13.6	93
	320	47.8	100	6.3	44
III	15	68.8	140	15.6	94
	20	62.2	108	11.1	77
	25	59.4	88	8.7	61
	30	55.8	64	6.0	43
	35	52.2	34	2.6	24
	45	49.8	17	1.7	13.5
	80	49.6	7.5	0.55	7.6
IV	15	63.6	134	14.4	89
	20	55.7	109	10.5	70
	25	52.8	80	7.7	52
	30	47.8	28	2.3	18
	35	47.8	24	2.0	14
	45	46.7	12	0.84	8
	80	44.8	7.2	0.44	4.8
V	15	76.7	151	18.6	ND
	40	67.8	136	14.7	96
	80	61.3	95	9.8	66
	130	56.8	65	5.9	43
	190	53.5	35	3.0	25
	250	52.2	28	2.5	20
	320	51.0	17	1.2	13.5

ND = not determined.

TABLE III (CONTD.)

ANALYSIS OF LABORATORY PULPS

Cook	Cooking Time, min.	Yield, %	Nu-Number	Klason Lignin, %	Kappa Number
VI	40	67.0	131	14.9	94
	50	65.2	114	12.8	79
	60	63.1	110	11.6	80
	70	62.1	104	10.6	73
	80	61.0	96	9.7	67
	90	60.2	91	8.9	65
	110	58.7	78	7.2	55
VII	20	70.0	131	14.4	96
	25	67.3	122	12.8	89
	40	61.5	85	8.0	55
	50	60.7	71	6.7	47
	60	58.3	55	5.0	36
	70	57.9	45	4.1	31
	90	55.5	24	2.3	19
	110	55.4	18	1.8	17
	140	54.5	12	1.5	12.6
VIII	20	72.8	326	25.4	151
	40	64.1	299	21.2	132
	60	57.5	237	15.4	106
	70	56.8	224	14.3	99
	80	53.4	188	11.3	80
	100	50.3	140	8.9	65
	110	51.8	147	9.1	66
IX	25	70.0	314	23.7	140
	40	61.2	300	21.7	135
	60	56.5	234	16.2	109
	70	54.3	213	14.7	101
	80	52.8	205	13.7	94
	100	48.6	139	8.7	62
	110	48.8	143	9.8	65
X	25	63.4	318	24.7	135
	40	57.9	277	19.6	126
	60	52.5	233	16.3	109
	70	51.0	209	13.1	91
	80	49.0	188	12.7	82
	100	47.3	140	9.6	66
	110	46.5	133	9.5	62

ND = not determined.

TABLE IV

ANALYSIS OF COMMERCIAL PULPS

Mill No.	Sample No.	Kappa No.	Klason Lignin, %	Nu-Number
1	1	29.2	3.85	50
	2	25.2	3.35	44
	3	25.6	3.40	44
	4	31.4	4.10	55
	5	31.4	4.05	52
	6	20.0	2.30	35
	7	30.6	3.90	54
	8	30.7	3.75	53
	9	30.1	3.80	51
	10	28.1	3.75	50
	11	27.2	3.40	45
	12	31.3	3.70	50
	13	28.4	3.35	48
	14	25.8	3.55	43
	15	28.6	4.00	47
	16	27.9	3.60	45
	17	27.4	3.50	47
2	1	64.1	9.75	98
	2	56.0	8.85	88
	3	53.0	8.40	84
	4	65.4	9.60	98
	5	53.0	7.60	85
	6	63.7	10.35	100
	7	67.1	10.60	104
	8	53.6	8.20	87
	9	60.0	9.30	96
	10	54.6	8.85	88
	11	73.8	11.60	110
	12	55.8	9.15	89
	13	46.7	7.45	75
	14	68.5	11.10	106
3	1	29.9	4.70	47
	2	32.7	5.25	51
	3	32.6	5.00	50
	4	30.9	4.75	49
	5	28.1	4.45	46
	6	26.1	4.20	44
	7	35.3	5.50	55
	8	37.6	6.05	59
	9	34.8	5.45	54
	10	29.7	4.75	48
	11	28.5	4.65	46
4	1	18.3	2.90	32
	2	25.8	3.95	37
	3	27.3	4.05	41
	4	42.1	6.60	62
	5	57.6	9.00	80
	6	23.7	3.55	37
	7	29.5	4.20	40
	8	29.2	4.20	39
	9	29.6	4.25	39
	10	27.2	4.05	38
	11	25.0	3.75	32
	12	22.3	3.40	31
5	1	52.2	7.70	81
	2	52.9	7.75	82
	3	41.7	6.25	67
	4	38.8	5.85	66
	5	48.7	7.15	73
	6	55.9	8.20	83
	7	63.3	9.25	90
	8	50.2	7.50	78
	9	54.7	7.55	79
	10	50.1	7.45	76
	11	39.2	5.80	60
	12	51.2	7.40	75
6	1	41.0	5.95	69
	2	41.0	6.10	74
	3	40.1	5.80	68
	4	42.1	6.35	75
	5	43.4	6.45	78
	6	46.3	7.15	85
	7	43.6	6.75	76
	8	39.1	5.70	71
	9	37.5	5.40	65
	10	38.7	5.60	67
	11	36.8	5.45	64
	12	37.3	5.40	61
7	1	99.4	14.80	151
	2	106	17.45	161
	3	91.7	13.65	145
	4	90.3	13.40	143
	5	98.1	17.20	155
	6	103	15.90	163
	7	110	17.25	170
	8	103	15.60	159
	9	109	16.95	158
	10	114	17.45	173
	11	104	15.70	163
	12	103	15.40	161

$$\% \text{ Klason lignin} = 0.15 \text{ Kappa no.} \qquad (2).$$

If the Nu-Number is a true measure of the lignin content of pulp, a similar relationship between it and both Kappa number and Klason lignin should exist. Using the data from Tables III and IV, the regression relationships between these three quantities were calculated for each species of wood used in the laboratory cooks, as well as for all softwoods combined. For the commercial pulps, similar calculations were made for the samples from each mill and for all of the samples combined. Tables V, VI, and VII show the results for the pulps produced in the laboratory, while Tables VIII, IX, and X show the results for commercial pulps.

Figure 8 is a pictorial summary of the data accumulated for commercial pulps, showing how changes in values for the three lignin methods are reflected in each other.

Modification of Procedure

The reasons for using ground pulp for the Nu-Number development work were that it was easier to weigh out the relatively small sample in this form; a more representative sample would probably be obtained, and it was necessary to grind the sample anyway for the Klason lignin determination. However, it would be obviously preferable to use the pulp directly without grinding, and so seven pulp samples from two different mills were used in comparing the Nu-Numbers of ground and unground dry pulp. The results are shown in Table XI.

Despite the apparent evidence that ground and unground pulps yield similar results, the 30-mg. sample size seemed too small to permit a great deal of confidence in the results. Accordingly, the procedure was modified further in a manner that would make it more easily applicable in a mill and would include a much larger pulp sample.

TABLE V

REGRESSION RELATIONSHIPS OF KLASON LIGNIN (KL) ON KAPPA NUMBER

(Laboratory cooks)

Wood	No. of Tests	Regression Lines	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
Loblolly	7	% KL = -1.90 + 0.168 Kappa	0.985	0.94	5.60	% KL = 0.151 Kappa	1.09	6.55
Black spruce	7	% KL = -3.72 + 0.186 Kappa	0.995	0.57	3.77	% KL = 0.152 Kappa	0.94	6.22
Southern pine	7	% KL = -2.80 + 0.182 Kappa	0.991	0.68	4.39	% KL = 0.154 Kappa	1.04	6.71
Douglas-fir	7	% KL = -2.42 + 0.184 Kappa	0.972	1.20	7.95	% KL = 0.158 Kappa	1.40	9.27
All softwoods	28	% KL = -2.71 + 0.180 Kappa	0.986	0.80	5.04	% KL = 0.153 Kappa	1.12	7.06
Aspen	36	% KL = -0.86 + 0.162 Kappa	0.997	0.32	4.55	% KL = 0.144 Kappa	0.38	5.40

TABLE VI

REGRESSION RELATIONSHIPS OF KLASON LIGNIN ON NU-NUMBERS

(Laboratory cooks)

Wood	No. of Tests	Regression Lines	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
Loblolly pine	7	% KL = -1.60 + 0.074 Nu	0.995	0.52	3.20	% KL = 0.0675 Nu	0.72	4.32
Black spruce	7	% KL = -4.11 + 0.086 Nu	0.987	1.02	7.54	% KL = 0.0678 Nu	1.07	7.75
Southern pine	7	% KL = -2.50 + 0.081 Nu	0.996	0.46	3.00	% KL = 0.0702 Nu	0.85	5.48
Douglas-fir	7	% KL = -2.12 + 0.080 Nu	0.985	0.90	5.96	% KL = 0.0710 Nu	1.02	6.75
All softwoods	28	% KL = -2.60 + 0.080 Nu	0.991	0.72	4.54	% KL = 0.0690 Nu	0.94	7.06
Aspen	36	% KL = -0.73 + 0.111 Nu	0.996	0.34	4.83	% KL = 0.101 Nu	0.42	5.95

TABLE VII

REGRESSION RELATIONSHIPS OF KAPPA ON NU-NUMBER

(Laboratory cooks)

Wood	No. of Tests	Regression Lines	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
Loblolly pine	7	Kappa = 1.60 + 0.440 Nu	0.998	2.83	2.58	Kappa = 0.447 Nu	3.03	2.75
Black spruce	7	Kappa = 2.41 + 0.432 Nu	0.997	2.93	2.93	Kappa = 0.444 Nu	3.28	3.28
Southern pine	7	Kappa = 3.70 + 0.438 Nu	0.997	2.15	2.13	Kappa = 0.450 Nu	2.45	2.43
Douglas-fir	7	Kappa = 3.55 + 0.428 Nu	0.992	3.50	3.66	Kappa = 0.447 Nu	3.66	3.85
All softwoods	28	Kappa = 2.18 + 0.438 Nu	0.997	2.28	2.24	Kappa = 0.447 Nu	2.32	2.28
Aspen	36	Kappa = 0.84 + 0.686 Nu	0.996	1.95	4.00	Kappa = 0.700 Nu	2.00	4.10

TABLE VIII

REGRESSION RELATIONSHIPS OF KLASON LIGNIN ON KAPPA NUMBER

(Commercial pulps)

Mill No.	No. of Tests	Regression Line	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
1	17	% KL = 0.14 + 0.123 Kappa	0.894	0.140	3.9	% KL = 0.128 Kappa	0.140	3.9
2	14	% KL = -0.23 + 0.160 Kappa	0.961	0.270	2.9	% KL = 0.157 Kappa	0.280	3.0
3	11	% KL = -0.14 + 0.162 Kappa	0.988	0.085	1.7	% KL = 0.157 Kappa	0.850	1.7
4	12	% KL = -0.28 + 0.160 Kappa	0.986	0.110	2.5	% KL = 0.151 Kappa	0.130	2.8
5	12	% KL = 0.58 + 0.135 Kappa	0.994	0.105	1.4	% KL = 0.147 Kappa	0.115	1.6
6	12	% KL = -1.66 + 0.189 Kappa	0.978	0.115	1.9	% KL = 0.148 Kappa	1.150	2.5
7	12	% KL = -2.15 + 0.176 Kappa	0.833	0.790	5.0	% KL = 0.155 Kappa	0.880	5.6
All Samples	90	% KL = -0.45 + 0.160 Kappa	0.998	0.270	3.5	% KL = 0.151 Kappa	0.300	4.0

TABLE IX

REGRESSION RELATIONSHIPS OF KLASON LIGNIN ON NU-NUMBER

(Commercial pulps)

Mill No.	No. of Tests	Regression Line	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
1	17	% KL = 0.108 + 0.073 Nu	0.872	0.21	5.8	% KL = 0.075 Nu	0.13	3.7
2	14	% KL = -2.14 + 0.123 Nu	0.966	0.34	3.7	% KL = 0.078 Nu	0.26	2.8
3	11	% KL = -0.875 + 0.117 Nu	0.987	0.09	1.8	% KL = 0.100 Nu	0.07	1.4
4	12	% KL = -0.406 + 0.116 Nu	0.989	0.26	5.8	% KL = 0.106 Nu	0.18	4.0
5	12	% KL = -1.37 + 0.115 Nu	0.975	0.22	3.0	% KL = 0.097 Nu	0.14	1.9
6	12	% KL = 0.360 + 0.080 Nu	0.954	0.18	3.0	% KL = 0.086 Nu	0.10	1.7
7	12	% KL = -4.10 + 0.126 Nu	0.795	0.90	5.8	% KL = 0.100 Nu	0.47	3.0
Total	90	% KL = -0.756 + 0.105 Nu	0.987	0.30	4.2	% KL = 0.091 Nu	0.19	2.6

TABLE X

REGRESSION RELATIONSHIPS OF KAPPA ON NU-NUMBER

(Commercial pulps)

Mill No.	No. of Tests	Regression Line	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
1	17	Kappa = -1.18 + 0.612 Nu	0.980	0.57	2.0	Kappa = 0.590 Nu	0.70	2.5
2	14	Kappa = -13.9 + 0.788 Nu	0.984	0.81	1.4	Kappa = 0.639 Nu	1.12	1.9
3	11	Kappa = -4.9 + 0.731 Nu	0.980	0.35	1.1	Kappa = 0.633 Nu	0.50	1.6
4	12	Kappa = -0.27 + 0.713 Nu	0.984	1.3	4.4	Kappa = 0.707 Nu	1.3	4.4
5	12	Kappa = -12.3 + 0.820 Nu	0.964	1.3	2.6	Kappa = 0.658 Nu	1.55	3.1
6	12	Kappa = 11.67 + 0.408 Nu	0.962	0.55	1.4	Kappa = 0.572 Nu	0.98	2.4
7	12	Kappa = 0.6 + 0.631 Nu	0.976	1.4	1.4	Kappa = 0.635 Nu	1.4	1.4
All samples	90	Kappa = 0.2 + 0.630 Nu	0.921	1.9	3.9	Kappa = 0.631 Nu	1.9	3.9

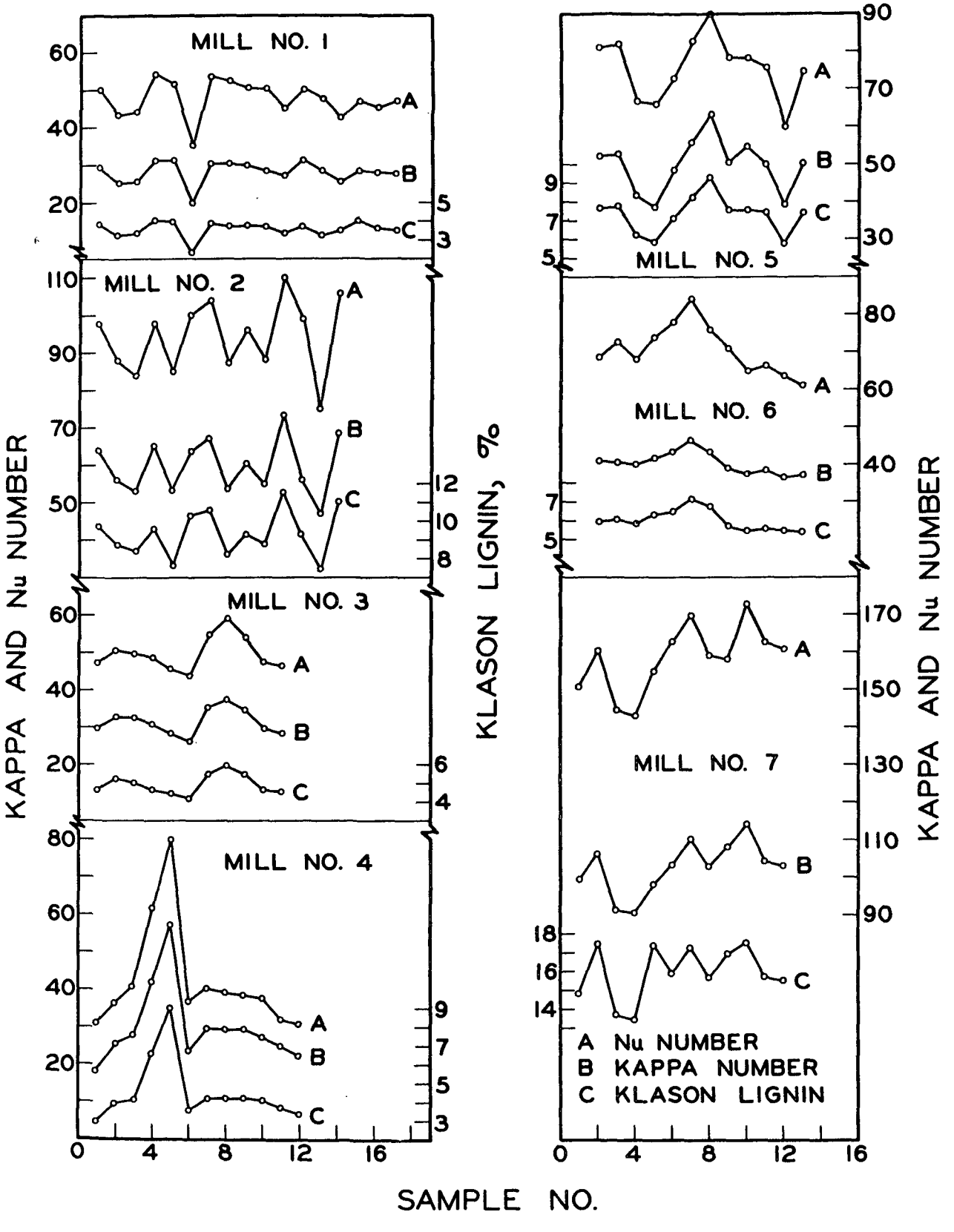


Figure 8. Results of Lignin Analyses for Commercial Pulps

TABLE XI

COMPARISON OF NU-NUMBERS OF GROUND AND UNGROUND PULP

Sample	Mill A Nu-Number		Mill B Nu-Number	
	Ground	Unground	Ground	Unground
1	32.7	30.0	177	180
2	41.0	45.8	172	170
3	46.0	48.7	165	159
4	41.4	41.0		
Mean	40.3	41.4	170	171

The modified procedure requires that a damp pad of pulp be made; its moisture content determined using a portion of it, and an amount of it weighed out in a 300-ml. beaker that is equivalent to 250 mg. o.d. pulp. Two hundred ml. of 14% HNO_3 are used, and the reaction temperature is 85°C. At this temperature, the reaction period will be 8-10 minutes for unbleached softwood kraft pulp. All other details of the procedure are as before. Figure 9 shows the relationship established between Kappa number and Nu-Number by applying this modified procedure to various samples of the commercial pulps listed in Table IV.

EXPERIMENTAL: OTHER PULPS

To explore the applicability of the Nu-Number test for lignin to pulps other than those cooked by the kraft process, magnesium-base sulfite and high-yield neutral sulfite cooks were made in the laboratory.

The sulfite pulps were produced from black spruce cooked for varying times at 145°C., using an 8:1 liquor-to-wood ratio. The liquor was composed of 59.8 g./l. total SO_2 and 22.7 g./l. $Mg(OH)_2$. Klason lignin, Kappa number, and Nu-Number were measured on all samples. The Nu-Number procedure used was that

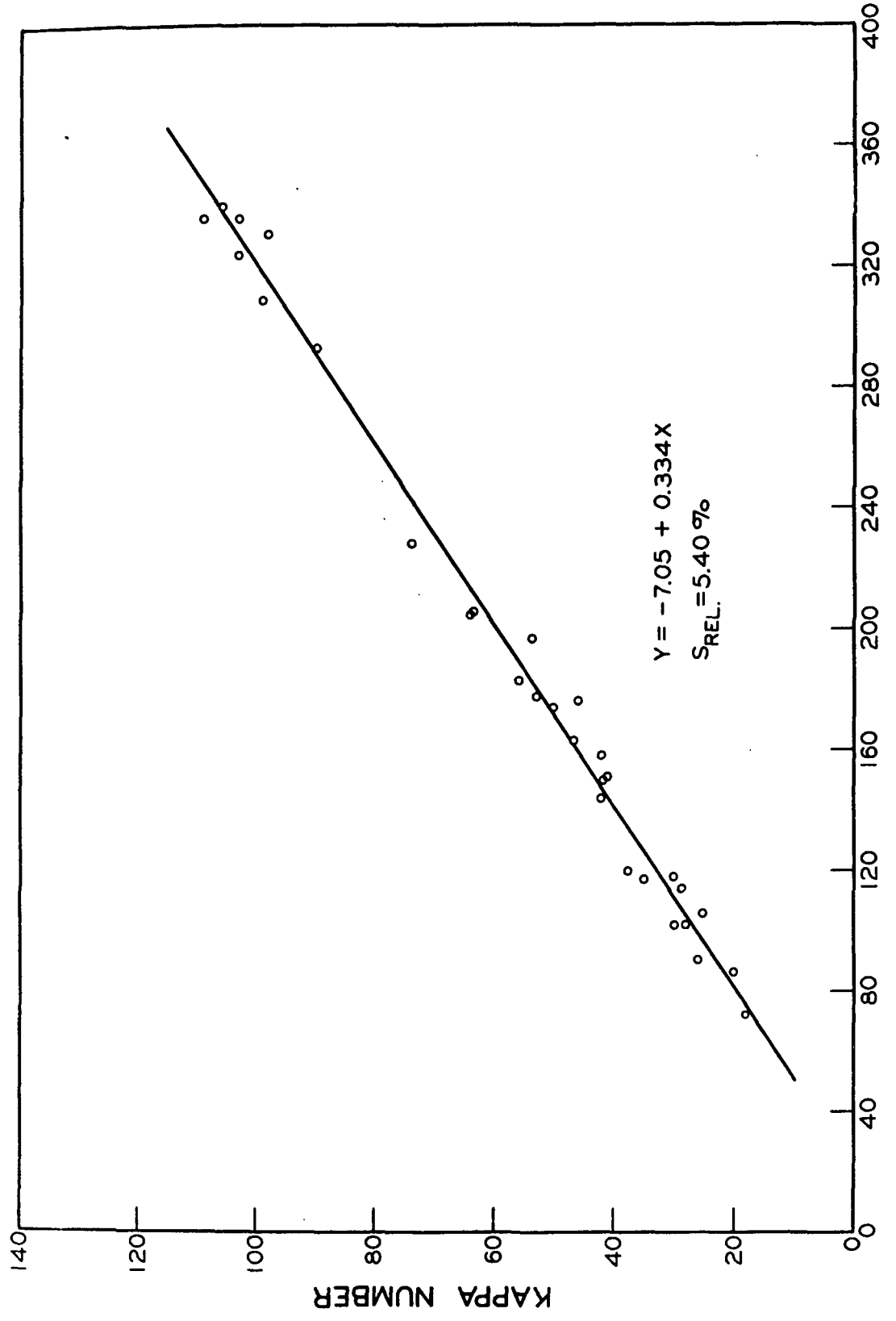


Figure 9. Relationship Between Kappa Number and Nu-Number for Unbleached Softwood Kraft Pulp Using the Modified Procedure

requiring 30 mg. of ground pulp. The analytical data are shown in Table XII. The Kappa numbers and Nu-Numbers were subjected to correlation analysis. The correlation coefficient was 0.996, the standard error of estimate was 2.7, and the relative error was 3.6%. In Fig. 10, Kappa number is plotted against Nu-Number the regression line is drawn through the data points, and the regression equation is given.

Similar to the Mg-base sulfite cooks, a series of neutral sulfite cooks were made at varying times to cover the desired yield range. The cooking temperature was 175°C., a 6:1 liquor-to-wood ratio was used, and the liquor composition was 15% Na_2SO_3 and 4% Na_2CO_3 (based on wood). Two species of wood were cooked separately: gum and aspen. The Klason lignin, Nu-Number, and yield values were determined on all pulps, and are shown in Table XIII. Klason lignin is plotted against Nu-Number in Fig. 11, and yield is plotted against Nu-Number in Fig. 12, where the regression line is drawn through the data points. The results of correlation analysis for the yield vs. Nu-Number data are given in Table XIV.

DISCUSSION

Laboratory Kraft Pulps

From Tables V and VI it is seen that the regression lines of Klason lignin on both the Kappa and Nu-Numbers show a negative intercept with the y-axis. This means that a pulp with no Klason lignin still possesses a positive Kappa and Nu-Number. This is probably due in both cases to reaction of permanganate and nitric acid, respectively, with the "acid-soluble" lignin not measured by the Klason method It can be shown statistically that these intercepts are highly significant, thus indicating that the line passing through the origin is significantly different from the calculated regression line. In this case, the use of the lines through the origin as an estimate of Klason lignin is an approximation only. This is also

TABLE XII

ANALYTICAL RESULTS FROM MAGNESIUM-BASE SULFITE PULPS

Cook	Yield, %	Klason Lignin, %	Kappa Number	Nu-Number
1	56.5	12.75	78.1	94
2	60.8	17.80	101	113
3	52.2	10.25	66.1	75
4	46.0	7.06	40.2	44
5	53.8	10.70	74.5	86
6	51.1	8.80	61.4	71
7	49.9	8.70	62.9	70
8	47.6	6.55	51.8	56
9	71.6	25.85	134	149
10	66.3	21.95	122	138
11	60.2	19.40	109	123
12	58.2	13.75	81.4	96
13	54.2	10.25	64.1	80
14	49.9	6.20	45.1	55
15	43.8	6.15	45.1	55

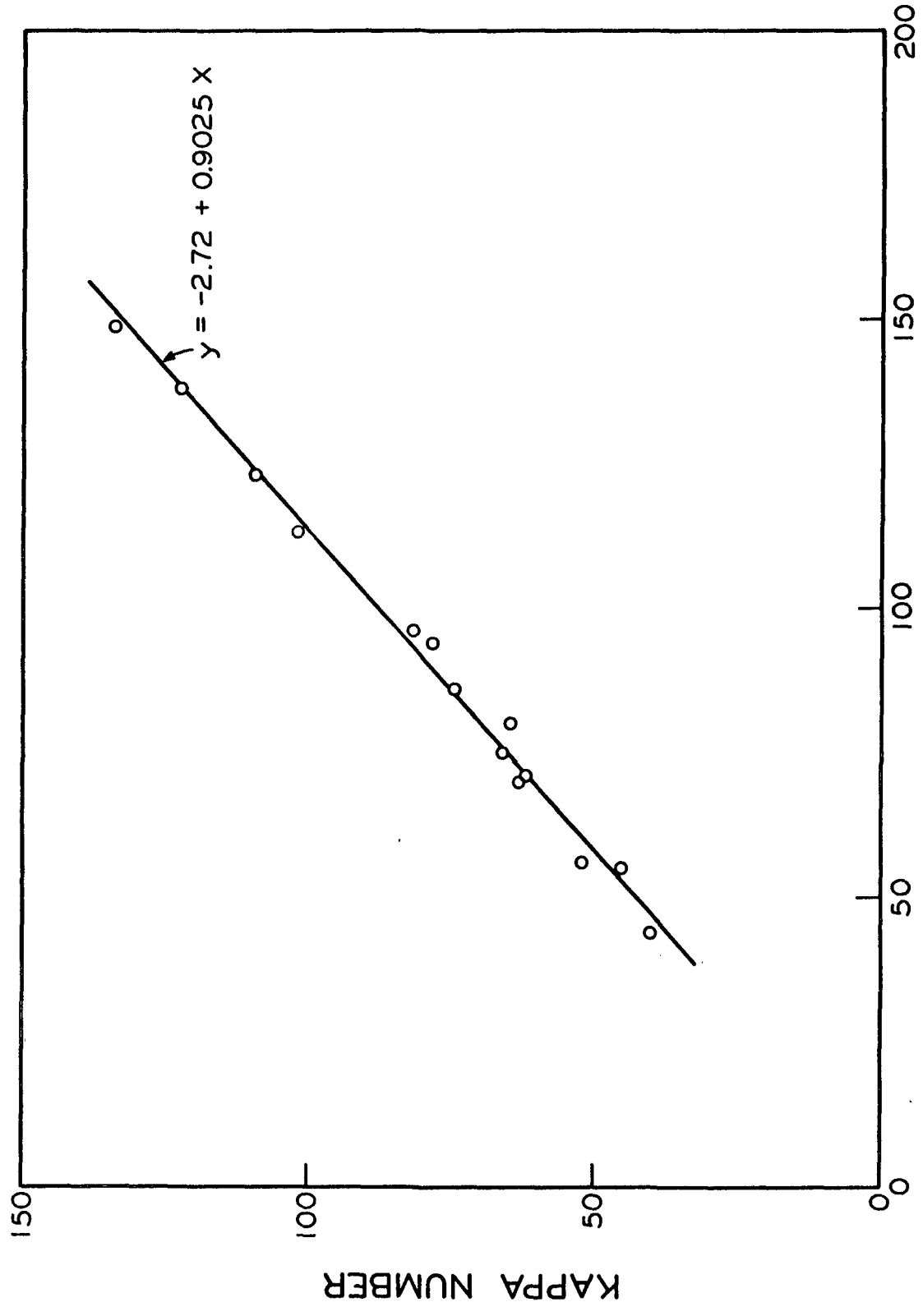
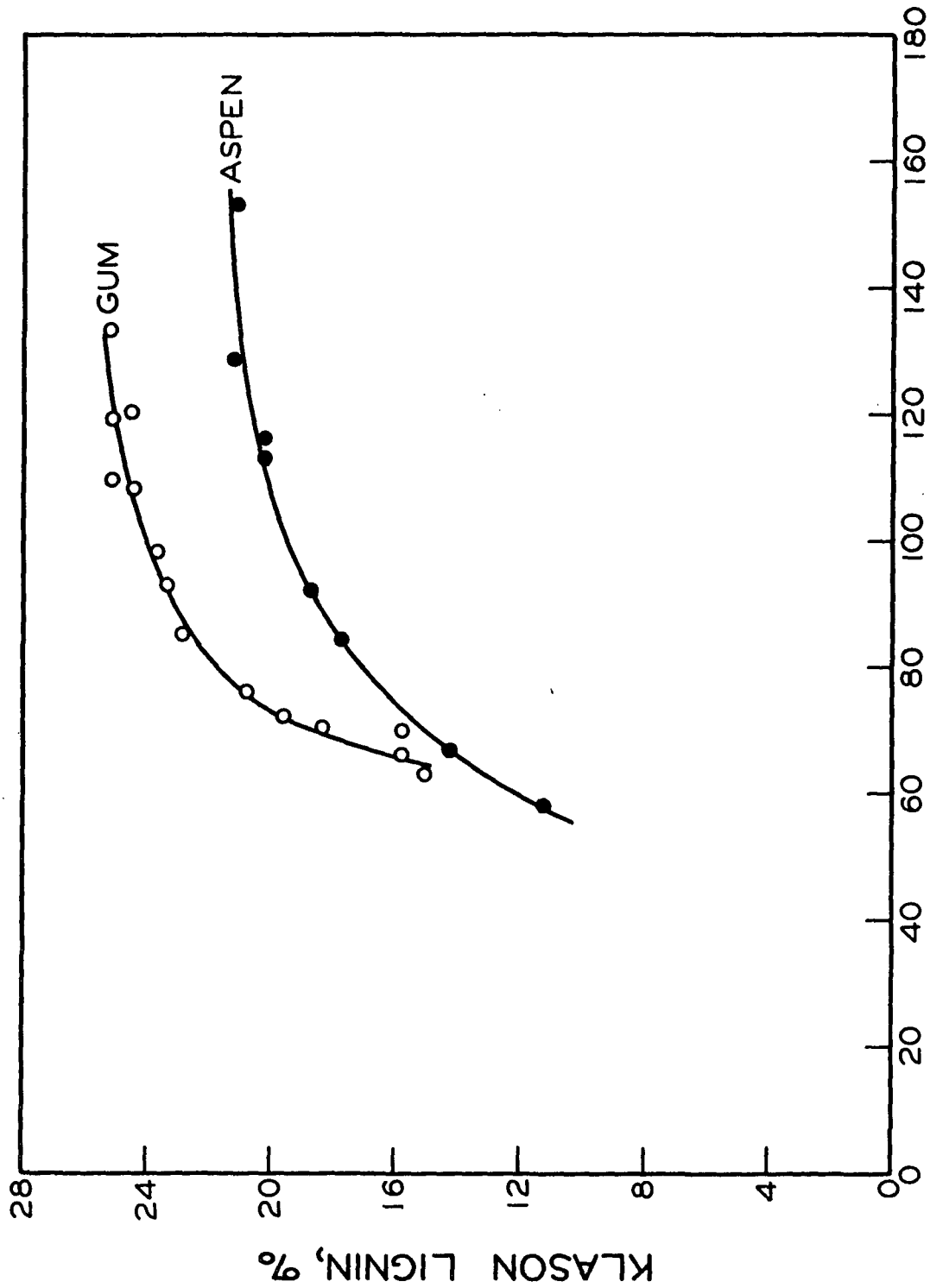


Figure 16. Magnesium Base Sulfite Pulping Kappa Number vs. Nu Number

TABLE XIII

ANALYTICAL DATA OF NEUTRAL SULFITE PULPS

Wood Species	Cooking Time, min.	Yield, %	Klason Lignin, %	Nu-Number
Gum	0 (wood)	100	25.10	133
Gum	7	90.8	24.45	120
Gum	12	89.3	25.07	119
Gum	17	87.2	25.05	109
Gum	20	85.4	24.40	108
Gum	25	78.0	23.65	98
Gum	30	74.3	23.35	93
Gum	40	76.0	22.80	85
Gum	55	65.0	20.70	76
Gum	90	62.3	19.55	72
Gum	130	61.0	18.25	70
Gum	200	55.8	15.75	70
Gum	250	57.5	15.80	66
Gum	300	56.4	15.10	63
Aspen	0 (wood)	100	21.10	153
Aspen	17	87.8	21.10	128
Aspen	22	83.3	20.20	116
Aspen	27	82.0	20.20	113
Aspen	41	78.6	18.75	92
Aspen	55	75.5	17.75	84
Aspen	150	67.7	14.25	67
Aspen	300	64.0	11.25	58



Kappa Number vs Nu-Number of Neutral Sulfite Pulps

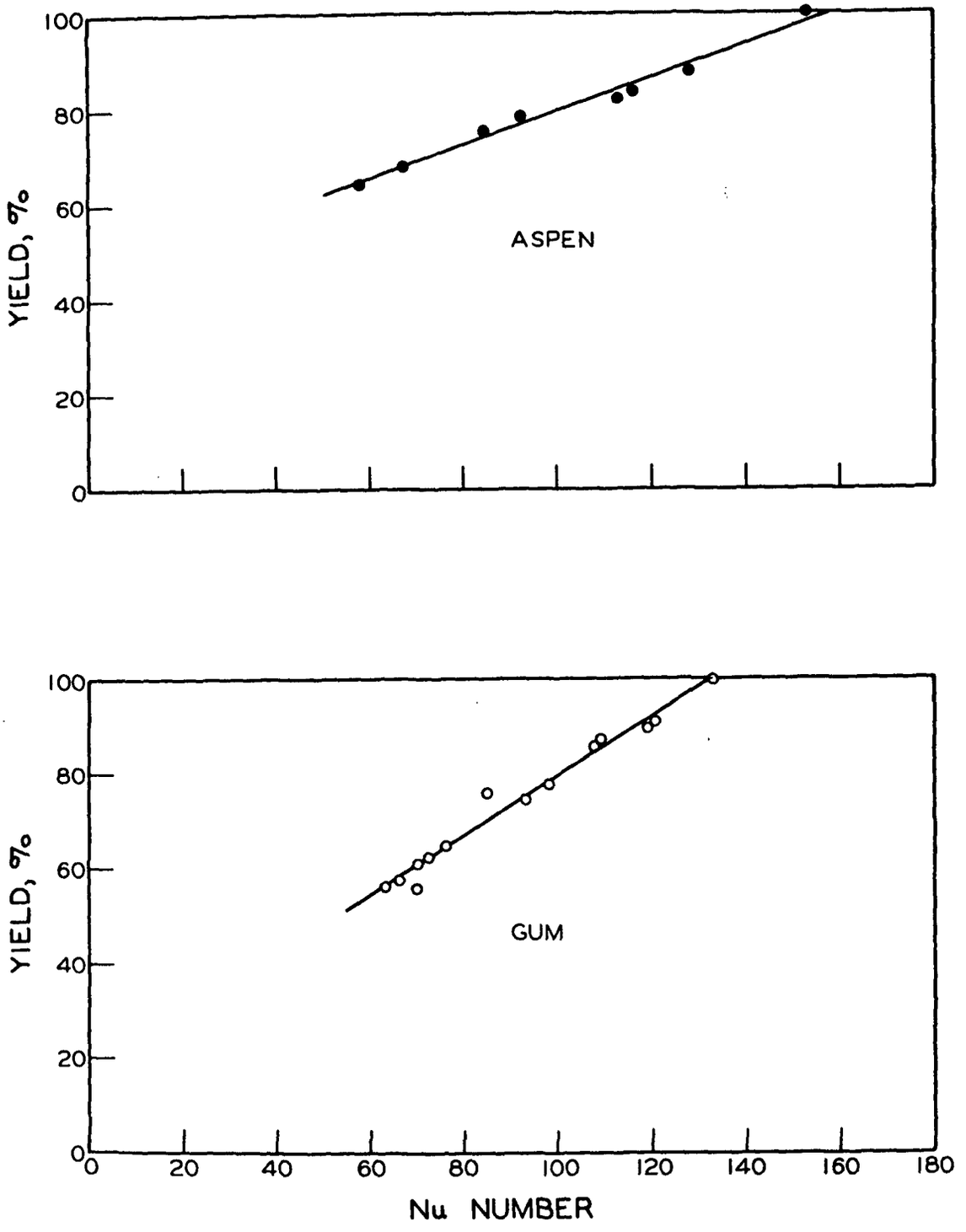


Figure 12. Percent Yield vs. Nu-Number of Neutral Sulfite Pulps

TABLE XIV

RESULTS OF CORRELATION ANALYSIS, NEUTRAL SULFITE PULPS

Wood	Cook	Regression Line	Corr. Coeff.	Std. Error	Rel. Error
Gum	N-S	Yield = 16.3 + 0.633 Nu	0.985	2.55	3.4%
Aspen	N-S	Yield = 44.7 + 0.347 Nu	0.980	2.20	2.7%

flected in the magnitudes of the standard error of the estimates calculated from th lines. From Table V it is seen that the standard errors are significantly gher for the estimates from the line through the origin.

It is further seen from Table V that the factors converting Kappa number Klason lignin are approximately the same for all softwoods and fairly close for pen, thus confirming Tasman's data that Kappa numbers generally can be converted percent Klason lignin by multiplying them by the factor 0.15. The factors con-ting Nu-Numbers to Klason lignin (Table VI) are also approximately the same for l softwoods. The factor for aspen, however, is significantly higher, thus icating that there exists no general factor for all pulps converting Nu-Numbers Klason lignin.

Table VII shows that the regression lines of Kappa on Nu-Number have itive intercepts. It can be shown statistically that these intercepts are y slightly significant, indicating that the straight line through the origin not significantly different from the regression line. In this case, the use the line through the origin, instead of the regression line, would introduce a slight additional error in the estimates. This is also reflected in the ndard errors of the estimates which are only slightly higher than those esti-d from the regression line.

These results show that at the conditions used in these experiments there linear relationship between Kappa and Nu-Number and that the regression line es through the point of zero Kappa-zero Nu-Number. Further, the results show the Kappa numbers may be estimated with an error of about ± 2.5% for softwoods about ± 4% for aspen.

The softwood cooks were performed under identical conditions. The as cooks, however, were performed under varying conditions, as shown in Table I. standard errors of estimate indicate that the variables introduced in this manne have no significant influence on the relationship between the Kappa and Nu-Numbe for aspen. It is reasonable to assume that this would be true with respect to softwoods also.

The conversion factor for Kappa number to Klason lignin was found to b approximately the same for both softwoods and aspen. This is not true, however for the factor converting Nu-Number to Kappa numbers, indicating that this facto must be determined in each case in order to express the results in Kappa numbers

The correlation coefficients show a high correlation between the three parameters. The correlation is more quantitatively expressed by the coefficien of determination, which is defined as the square of the correlation coefficient. This quantity is used to determine the percentage variation in the dependent var able caused by errors in the independent variable. Applying this quantity to t results, it is found that in more than 98% of the cases a variance in the Kappa number is reflected in the Nu-Number.

Commercial Kraft Pulps

Table X shows that the intercepts of the regression lines of Kappa on N Numbers vary from negative to positive values. The intercepts of the regressio lines of Mills 1, 3, 4, and 7 are not significantly different from zero, while th other intercepts are definitely significant. However, the standard error of est mates from the lines through the origin have only slightly higher values than tho estimated from the regression lines, thus indicating that if the lines through th

origin instead of the regression lines are used for obtaining estimated Kappa numbers from experimental Nu-Numbers, only a slight additional error is introduced. It is noted from Table IV that the Kappa and Nu-Numbers from each mill cover a very narrow range (max. 20 Kappa) compared with the ranges covered in the laboratory cooks (15-140). Consequently, any errors in the determination of the two parameters will influence the slope of the regression line to a greater extent for the mill samples than for the laboratory pulps.

However, when all the samples are considered together, the Kappa number range is considerably increased (18-110) and the regression relationship based on these data give a better estimate of the true relationship between the two parameters. In Table X are shown the regression relationships calculated on this basis. It is seen that this line does not differ significantly from the line through the origin, indicating that the true regression line, shown in Fig. 13, passes through the origin.

The samples used in this study were chosen to represent different kinds of softwoods, digester types, and locations. Table II shows that although the cooking conditions varied somewhat, as a whole, the samples may be considered fairly representative of pulp produced by the kraft process.

It can be seen that the development of the Nu-Number method has been based on its correlation with two other methods of lignin determination: the Kappa number method and the Klason lignin method. All three procedures were applied to the commercial pulps, and the analytical results summarized in Fig. 8. These three methods have their own limits of precision, as illustrated by the standard deviations shown in Table XV.

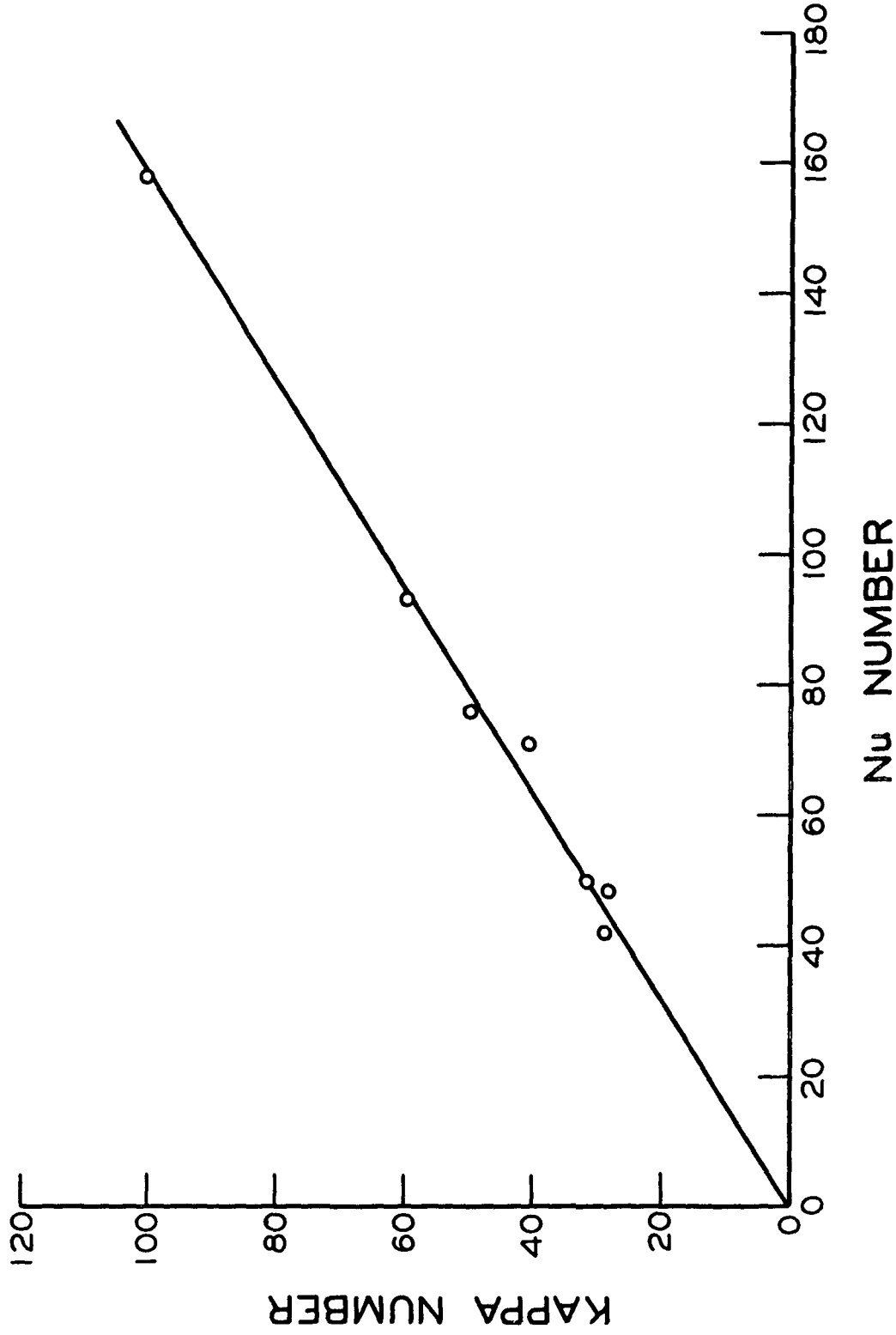


Figure 13. Mean Regression Relationship of Kappa Number on Nu-Number for Commercial Pulps

TABLE XV

STANDARD DEVIATIONS FOR THE THREE METHODS USED FOR MEASURING LIGNIN IN PULP

Test	No. of Tests	Mean Value	S, %	$S_{Rel.}$, %
Kappa number	58	61.6	0.55	0.9
Nu-Number	36	121	2.1	1.7
Klason lignin	55	10.7	0.35	3.3

Neutral Sulfite and Mg-Base Sulfite Pulps

To date, investigations of the applicability of the Nu-Number test for determination of lignin in sulfite and neutral sulfite pulp have been much less extensive than those for kraft. For sulfite pulp, the results shown in Fig. 10 indicate a linear relationship between Kappa number and Nu-Number, a result that seems to warrant further investigations.

The very limited data available for neutral sulfite pulps show that the relationship between Klason lignin and Nu-Number has little practical significance in the yield range investigated. The strictly empirical relationship between yield and Nu-Number indicates the possibility that the test may have some use as a measure of yield in high-yield pulping. However, it can be seen that different species grossly affect the yield–Nu-Number relationship. Thus, when applied to pulp derived from cooking mixed hardwoods, a significant change in the composition of the mixture would probably alter this relationship. Yet the data obtained so far are of sufficient interest to prompt further work.

Modified Nu-Number Procedure

The initial procedure, requiring 30 mg. of pulp, 50 ml. of 14% HNO_3, and a reaction temperature of 70°C., led to results that correlated very well with the Kappa number, that is, the regression line relating the two parameters had a zero intercept. As shown in Fig. 9, the modified procedure yields a relationship wherein a negative Kappa value is obtained at zero Nu. The ratio of pulp to nitric acid apparently has a considerable effect on the slope and intercept of the regression relationship, as indicated in Fig. 14, where the same unbleached kraft pulps were used in both series of tests. That a zero Kappa-Nu intercept is not obtained by the modified procedure does not, however, destroy the validity of the relationship or its usefulness in converting Nu to Kappa.

The relative standard error of estimate ($S_{Rel.}$) of 5.4% shown in Fig. 9 is somewhat higher than that associated with the earlier procedure. This is most likely attributable to procedural uncertainties such as in the moisture determination of the pad from which the sample is taken.

The Lignin-HNO_3 Reaction

The reaction of nitric acid with lignin in pulp is, as in all lignin chemistry, a difficult one to assess. However, some insight may be gained from an examination of the literature on the subject and from experiments performed during development of the method. The absorption maximum at about 425 nm., shown in Fig. 1, is evidently due to an intermediate product since it is shown by the reaction rate curves in Fig. 4-7 that it goes through a maximum intensity. Additional experiments have shown that this absorption maximum finally disappears upon prolonged heating. The peak at about 340 nm., however, increases in absorption intensity during prolonged reaction.

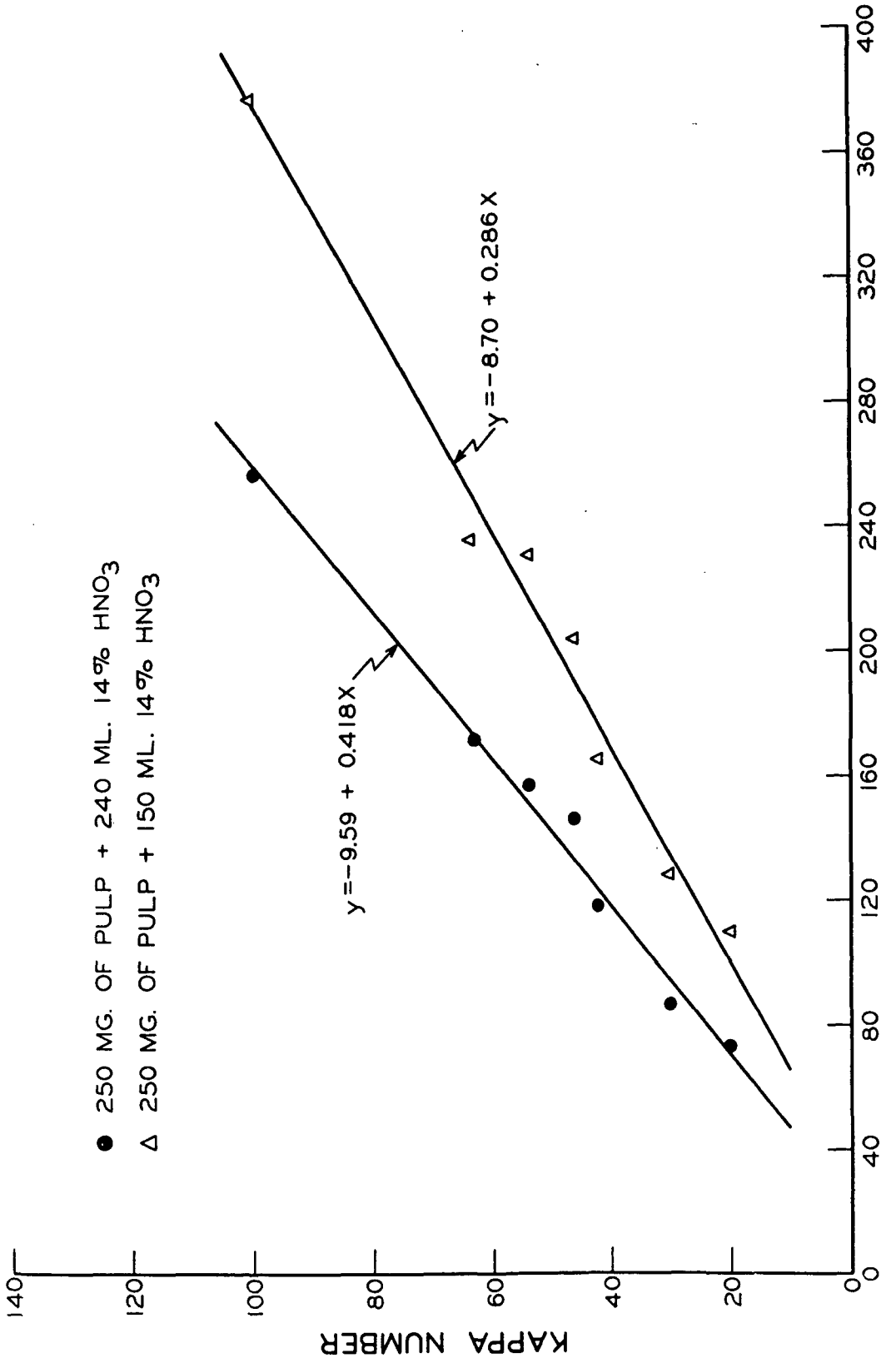


Figure 14. Effect of Pulp:HNO_3 Ratio on Kappa-Nu Relationship

At the same time, the existence and height of the 425-nm. peak, or shoulder, is a function of the nitric acid concentration, as illustrated in Fig. 15. The data in Fig. 15 were derived by scanning from 320 to 600 nm. the filtered liquid phase following heating 30 mg. of ground pulp for 30 minutes with 5, 10, 14, 20, 30, 40, 50, 60, and 70% HNO_3, respectively. The results show, too, that the absorbance at 425 nm. is at a maximum when 14% HNO_3 is used, and agrees with Kalisch's (20) statement that high acid concentrations favor oxidation while low ones favor nitration.

Bartunek obtained the peak at 340 nm. upon reaction of phenol with nitric acid, an indication that the product causing the peak is an aromatic nitro compound. There is some evidence that nitrous acid is a catalyst in this reaction. Sobolev (21) has shown that when 4-methyl guaiacol, a simplified lignin model with no side-chain oxygen, is treated with 16% aqueous nitric acid at 70°C., 4-methyl-nitroso-guaiacol is formed as a first intermediate. He suggested that the reaction proceeds by the special nitration mechanism described by Ingold and coworkers (22). Accordin to this mechanism, initial attack on the aromatic nucleus is by nitrosium ion (NO^+) derived from molecular nitrous acid (which is always present in concentrated nitric acid):

$$HNO_2 + HNO_3 \rightleftarrows H_2NO_2^+ + NO_3^- \quad (3),$$

$$H_2NO_2^+ \rightleftarrows NO^+ + H_2O \quad (4),$$

$$NO^+ + NO_3^- \rightleftarrows N_2O_4 \quad (5),$$

$$ArH + NO^+ \rightarrow ArNO + H^+ \quad (6),$$

$$ArNO + HNO_3 \rightarrow ArNO_2 + HNO_2 \quad (7).$$

Sobolev was able to show that the reaction was inhibited by adding urea which destroys the nitrous acid. This inhibiting effect was confirmed by this work when,

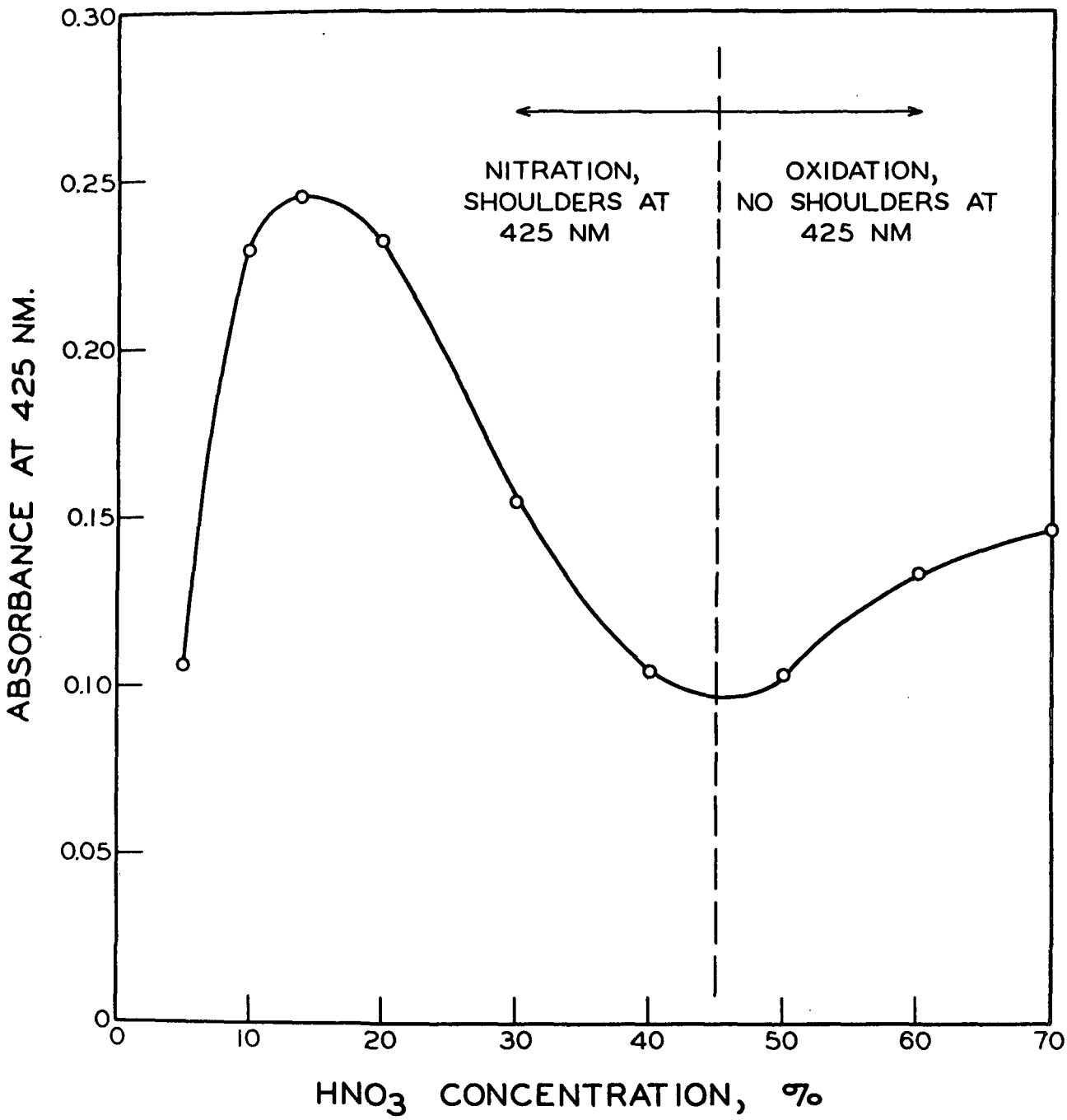


Figure 15. Absorbance at 425 nm. of Product from Reaction of Nitric Acid with Unbleached Kraft Pulp, as a Function of Nitric Acid Concentration

upon adding a small amount of urea to the nitric acid, the spectrum of the filtere reaction mixture failed to show a peak at 425 nm.

The species absorbing at 425 also appears similar to the nitration produ of coniferyl alcohol, as shown by brief experiment. One mg. of coniferyl alcohol was heated for 15 minutes at 70°C. with 50 ml. of 14% HNO_3, and the reaction mixtu was then scanned from 320 to 570 nm. Figure 16 shows this scan along with a simi lar one for pulp-HNO_3. The spectra are nearly identical.

In summary, it appears that the yellow, soluble substance produced by reaction of pulp with 14% nitric acid may be a nitro derivative of a lignin unit o the type isolated by Sobolev with the side chains intact.

CONCLUSIONS

The method of lignin determination called Nu-Number method is applicable unbleached softwood kraft pulp, unbleached hardwood kraft pulp, and Mg-base unblea softwood pulp. It has not yet been shown to be as precise as the Kappa number method, but the indications are that with further work and a more carefully standa ized procedure it may be shown.

Because of the use of only a single reagent, which it is not necessary t standardize, and because of the final color measurement by a photometer, convenien of application and objectivity of results may be of a higher order than the method presently employed in mill pulping and bleaching control.

Full extension of the method to pulps derived from various processes, an to pulps in intermediate stages of processing, such as in various stages of bleach awaits further study.

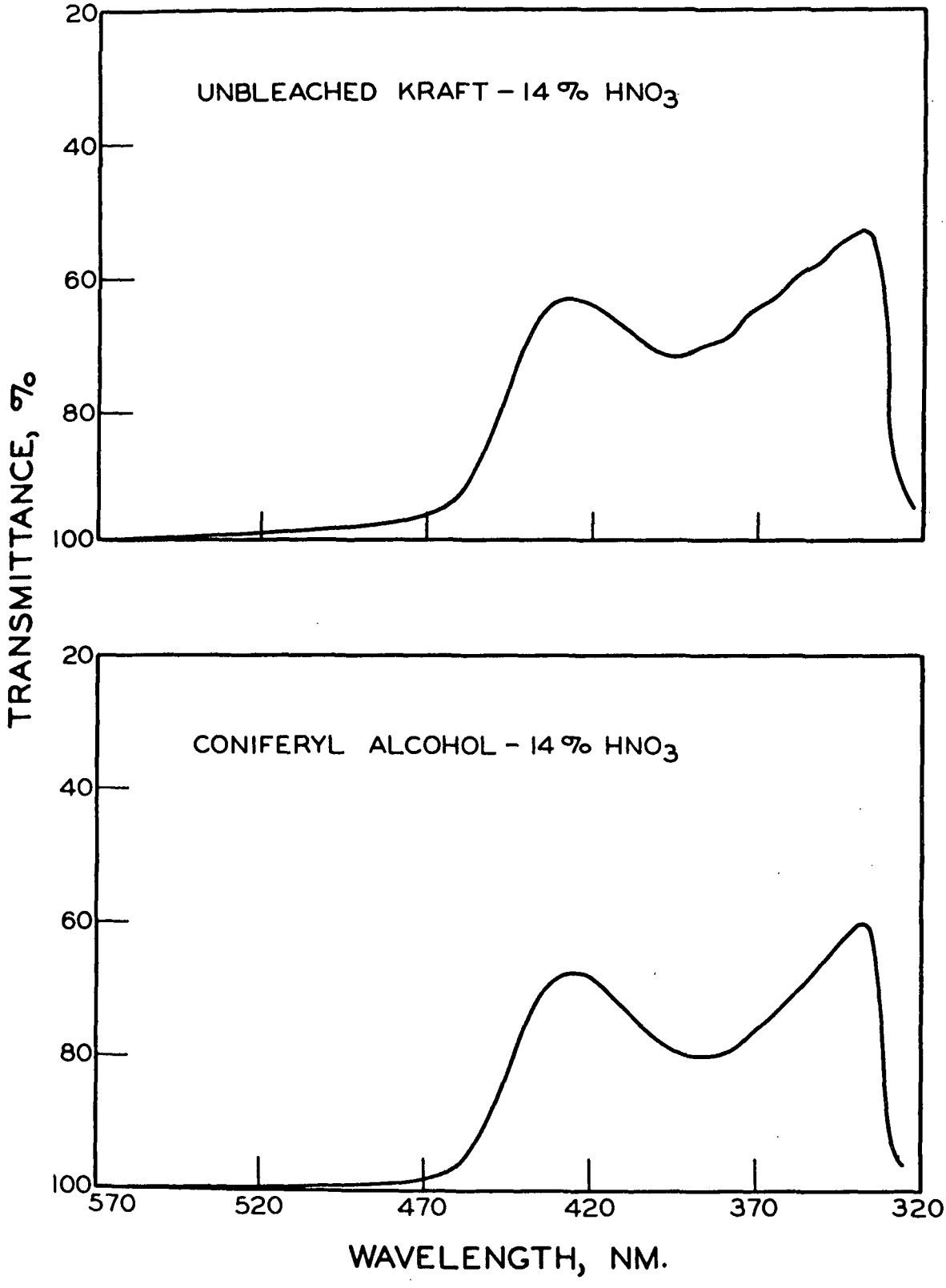


Figure 16. Absorbance Spectra of Products from Reaction of Nitric Acid with an Unbleached Kraft Pulp and with Coniferyl Alcohol

MEASUREMENT OF DRY FIBER CONTENT OF AQUEOUS SUSPENSIONS OF COMPRESSIBLE FIBROUS MATERIALS

THEORETICAL BASIS

A device has been developed for the indirect measurement of the mass of moisture-free, compressible material in a selected volume of a water suspension of that material. The theoretical basis of the device is expressed by the "compressibility function,"

$$\log C = \log m + n \log P \qquad (8),$$

or

$$C = mP^n \qquad (9),$$

where:

$\underline{C}$ = mass of moisture-free, compressible material in a water-saturated, confined, compressed bed of that material,

$\underline{P}$ = the compressing pressure, and

$\underline{m}, \underline{n}$ = experimental constants.

In studies of the sheet-forming process during papermaking, the compressibility constants, $\underline{m}$ and $\underline{n}$, are required in calculations of the specific surface area and the specific volume of papermaking fibers, along with constant-rate filtration resistance data. The procedure and apparatus commonly used to measure the compressibility were devised by Ingmanson (23, 24) and further developed in other investigations by Ingmanson and coworkers (25, 26). The apparatus is shown in cross section in Fig. 17.

After flooding the septum with water from the 500-cc. water reservoir, a slurry containing about 5 g. of pulp is poured into the cylinder with the cover and piston removed. Sufficient water is added to position the water level about an inch below the cylinder top, and the slurry is then briefly stirred with a stirring

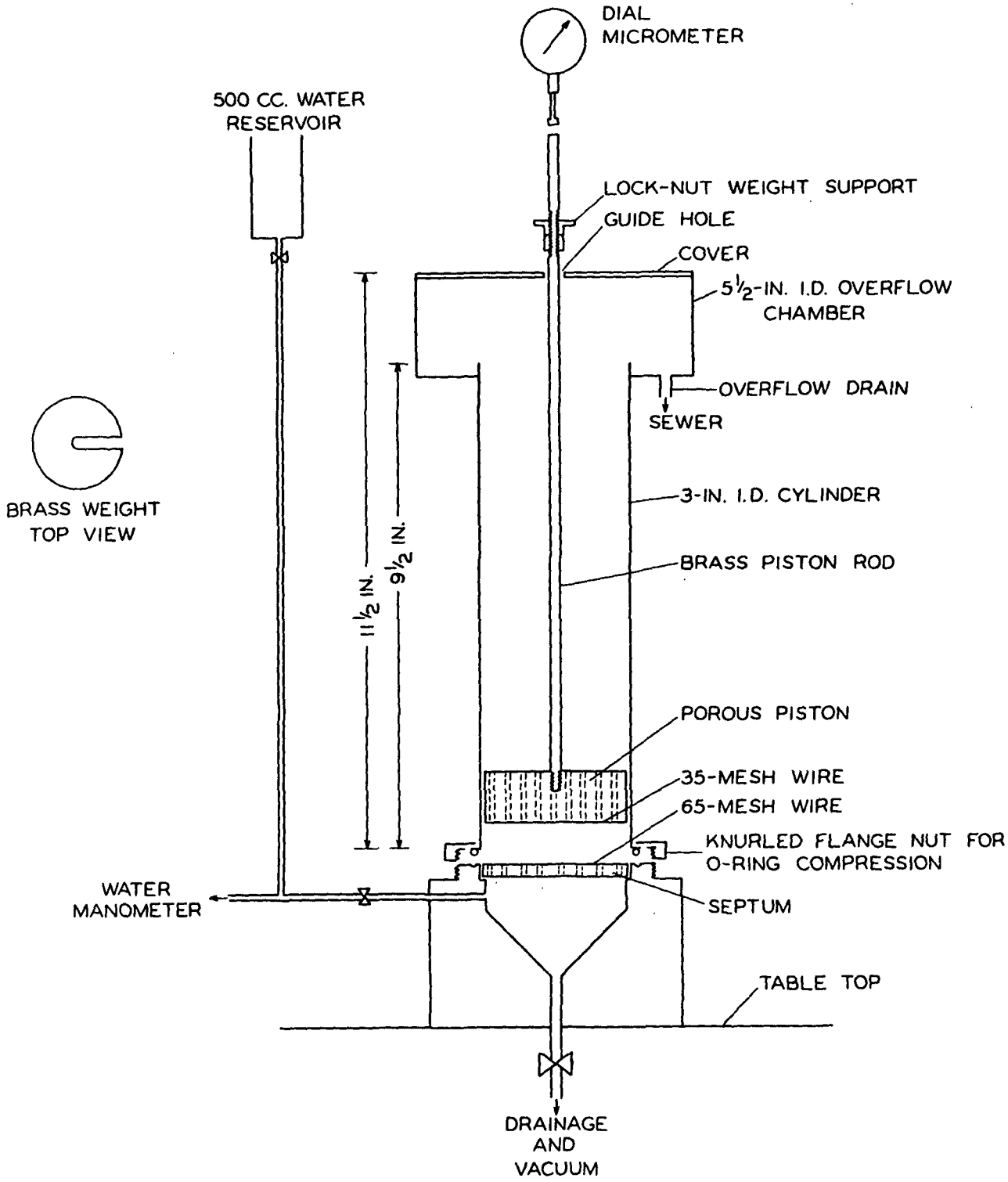


Figure 17. Laboratory Compressibility Apparatus

rod. The piston and the cover to the overflow chamber are inserted and the piston is lowered gently by hand. When the piston rests upon the fibers, now formed into a loose mat, it is released and the dial micrometer, which is on a swing arm, is placed over the piston and its foot is placed on top of the piston rod. The piston and piston rod assembly, having a known mass, form the first weight. When the micrometer foot is placed on the piston rod, a timer is started, and at the end of 12 minutes, the micrometer is read, giving the distance between the piston face and the septum face, which is the pad thickness. At the start of each run, the micrometer is, of course, zeroed with the piston in place and with nothing in the cylinder.

At the end of the 12-minute period, a brass weight similar to the one shown in Fig. 17 is placed on the piston rod so that it rests on the lock nut, and after another 12-minute period the micrometer is read again. This procedure is repeated with five more weights of increasing mass. After the last reading of the micrometer, the water in the cylinder is drained through the piston and the fiber mat, and the piston is removed from the cylinder. The cylinder assembly is detached from the septum assembly and remaining water is drawn from the pad by applying vacuum to the bottom of the septum. The pad is quantitatively removed, placed in a tared weighing bottle, dried at 105°C., and weighed.

From the experimental data (the known mass of each weight, the pad thickness determined by each micrometer reading, and the final dried pad weight), the solids concentration as a function of compacting pressure is established from Equation (10):

$$C_p = \frac{W}{AL} \qquad (10)$$

where:

C_p = solids at pressure P (P given by the applied weights), g./cc.,

W = dried pad weight, g.,

A = empirical constant, and

L = measured pad thickness.

If $\log C_p$ in g./cc. is plotted against $\log P$ in dynes/cm.^{2}, it will be found that the relationship is linear, as illustrated in Fig. 18.

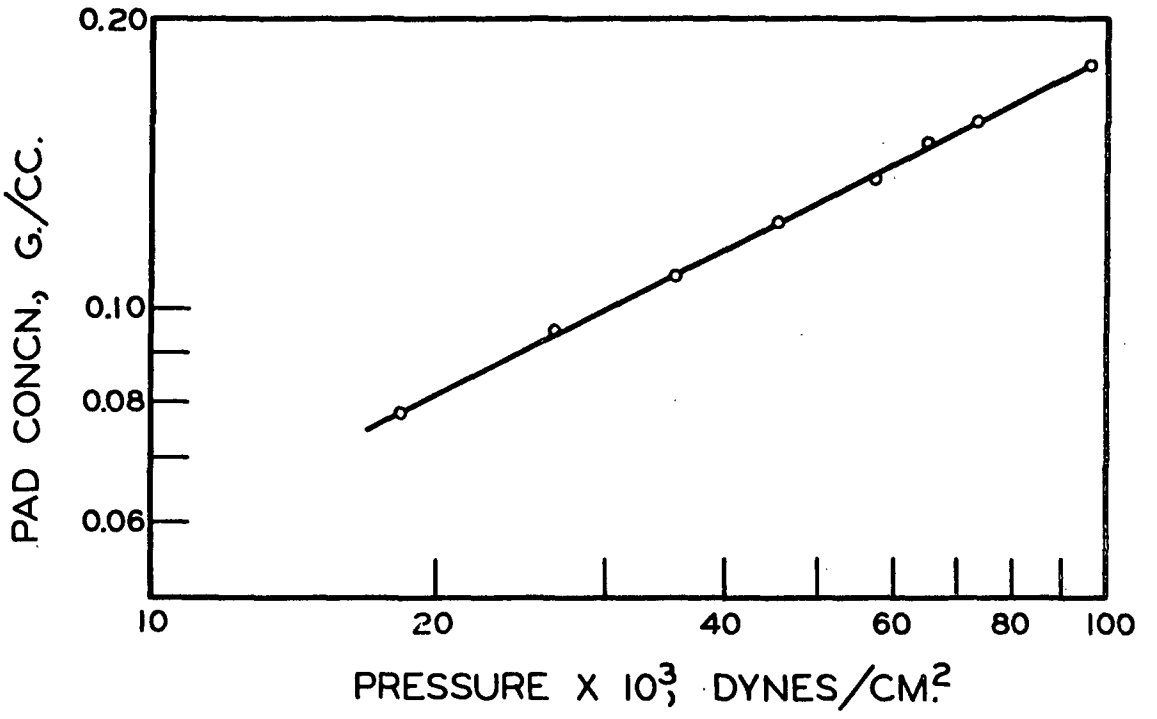


Figure 18. Relationship Between Dry Fiber Concentration of a Compressed Bed of Kraft Pulp and the Compressing Pressure

It can be seen that this procedure requires a minimum of an hour and a half to complete and is performed for purposes entirely different from that of measuring the amount of fiber in the slurry. In fact, the amount of fiber used is measured subsequent to the test, by removing the pad from the apparatus, drying it, and weighing it. The present procedure and apparatus were, of course, developed as a tool for laboratory investigation of certain pulp properties.

ESTABLISHMENT OF $\underline{W}$ VS. $\underline{L}$ RELATIONSHIP

Equation (10) can be rearranged to the form

$$W = C_p AL \qquad (11),$$

illustrating more clearly a direct relationship between $\underline{W}$ and $\underline{L}$. $\underline{A}$ is a constant reflecting the geometry of the system in which the fiber pad is compressed, fiber structure and composition, and certain physical and mechanical conditions under which the test is made. $\underline{C_p}$ is by definition a constant at pressure $\underline{P}$. Therefore, at constant compressing pressure, $\underline{C_p}$ is constant and can be combined with $\underline{A}$ to yield an even simpler equation,

$$W = AL \qquad (12),$$

showing clearly that the weight of dry fiber in a compressed, water-saturated pad at constant compacting pressure and constant cross-sectional area is a direct, linear function of the pad thickness.

Using the apparatus shown in Fig. 17 and the procedure described for its use, the validity of Equation (12) was tested, using a slurry of unbleached kraft pulp that had a Kappa number of 54. Varying amounts of the pulp were placed in the compressibility apparatus and the six weights were placed upon the piston at 12-minute intervals, the final pad thickness being read when the rate of compression reached an "equilibrium" value of 0.001 inch per minute. The data are illustrated in Fig. 19. The regression equation was found to be:

$$W = 0.19 + 15.8L \qquad (13).$$

This regression line is drawn through the data points in Fig. 19. The correlation coefficient is 0.9998, and the standard error is 0.025 g., which gives a relative error of 1.1%.

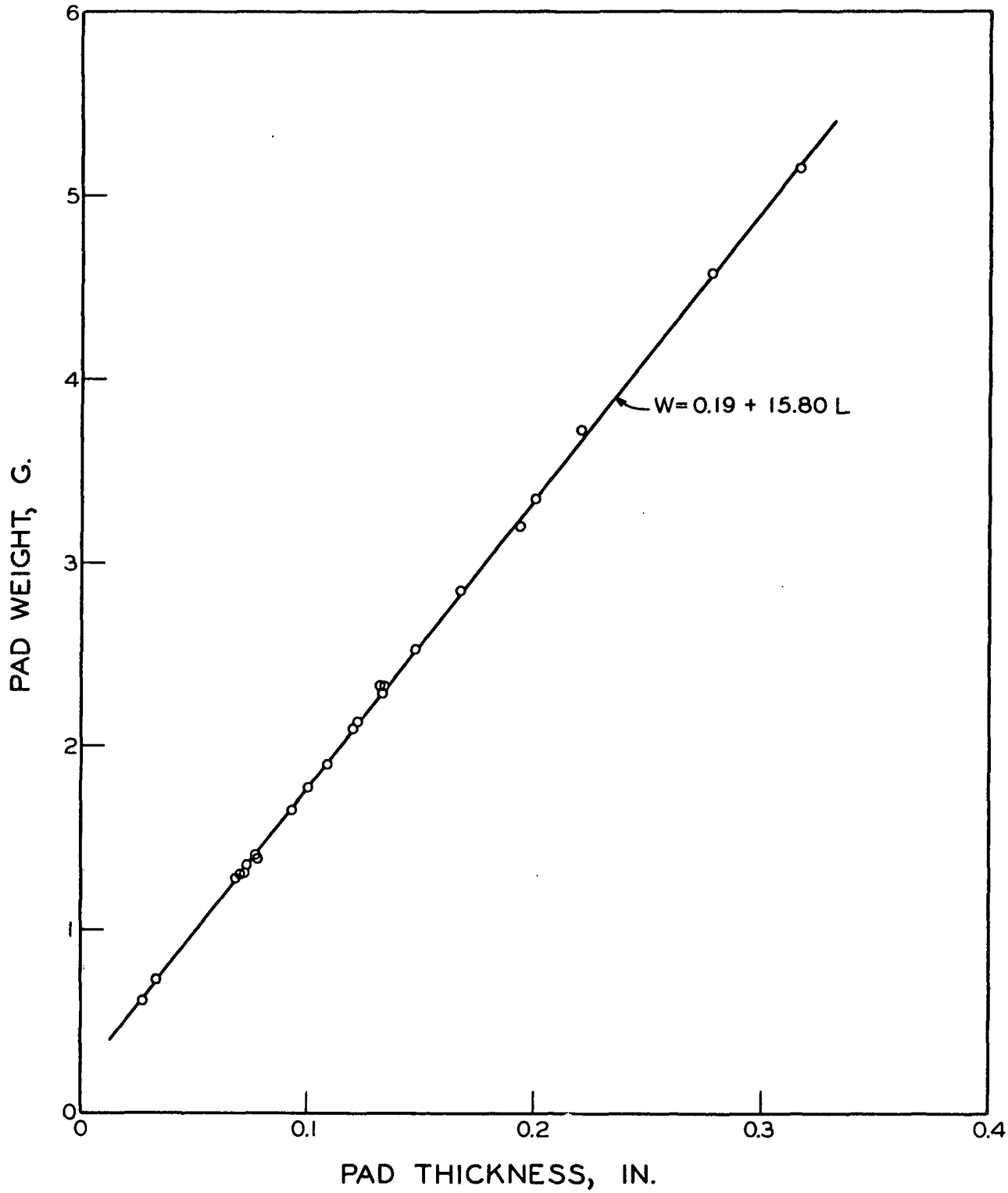


Figure 19. Pad Weight vs. Pad Thickness at 146 x 10^{-3} Dynes/Cm.^{2}

Using the same pulp, another series of experiments were made in which the total weight, corresponding to a pressure of 37.7×10^3 dynes/cm.^{2}, was placed on the piston at once. These results are plotted in Fig. 20. The regression equation is:

$$W = 0.070 + 10.70L \qquad (14) .$$

The standard error is 0.029 g. and the relative error is 1.85%. The correlation coefficient is 0.9996.

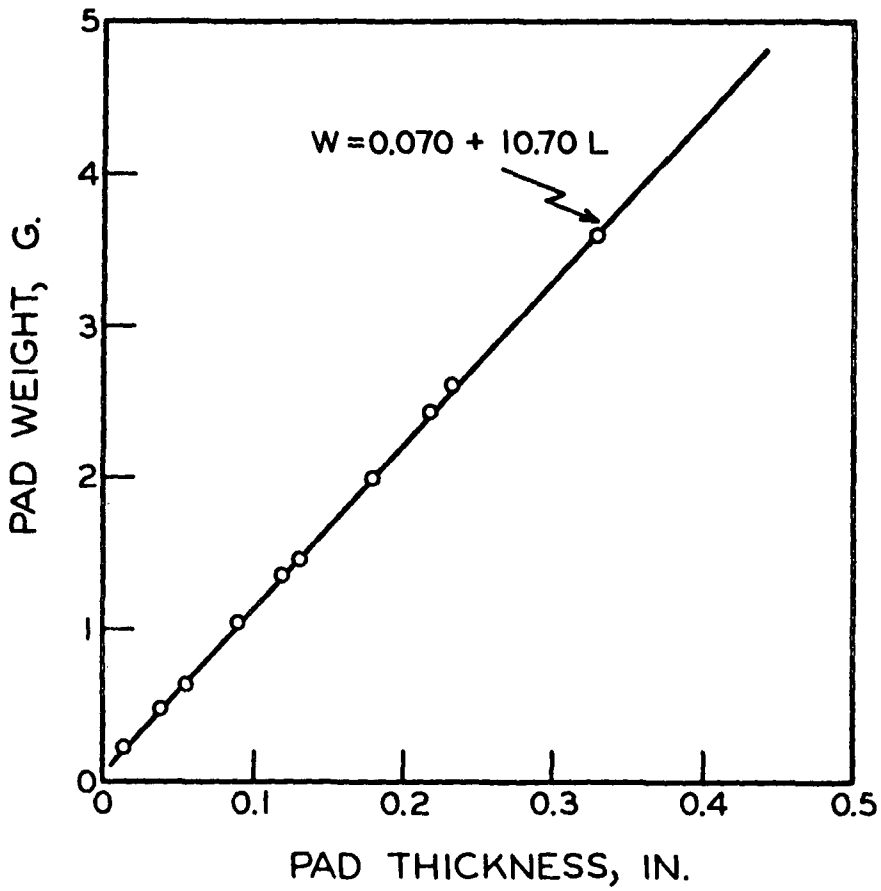


Figure 20. Pad Weight vs. Pad Thickness at 37.7×10^3 Dynes per Cm.^{2}; Weight Added at Once

Figures 19 and 20 contain experimental evidence that a linear relationship exists between the thickness of a compressed pad of fibers and the dry fiber content of the compressed pad under static load conditions, as predicted by Equation (12). It can also be seen that the precision with which the dry fiber content can be estimated from thickness measurements is within an error of 2%. It was found in these experiments that the time required to reach the arbitrarily chosen "equilibrium" compression rate of > 0.001 in./min. is a direct function of pad thickness.

The significance of the time to "equilibrium" and of the precision of estimating dry fiber content from thickness measurements can be seen from a consideration of possible design features of an automated apparatus. After introduction of a fixed volume of pulp slurry into the cylinder of such an apparatus, the weighted piston could be lowered at a controlled rate until a fiber pad forms. At this point, the weighted piston could be released to compress the pad to the equilibrium rate of compression, at which point its thickness would be measured. Once the slurry is in the cylinder, the whole process should not take more than three minutes if "thin" pads are formed.

DESIGN AND TESTING OF SMALLER SCALE, HIGH-TEMPERATURE APPARATUS

Having satisfactorily established, both theoretically and experimentally, the relationship between pad weight and pad thickness, an apparatus was designed, built, and tested that can be used at temperatures approaching the boiling point of water and that is resistant to the action of certain corrosive chemicals. The materials of construction consist primarily of pyrex, stainless steel, and polysulfone plastic. The assembly is shown in cross section in Fig. 21.

The pyrex cylinder is 9 inches long, 1.0100 ± 0.0002 in. i.d., and 1.16 in. o.d. It is enclosed by a water jacket made of 2.75-in. o.d. pyrex tubing.

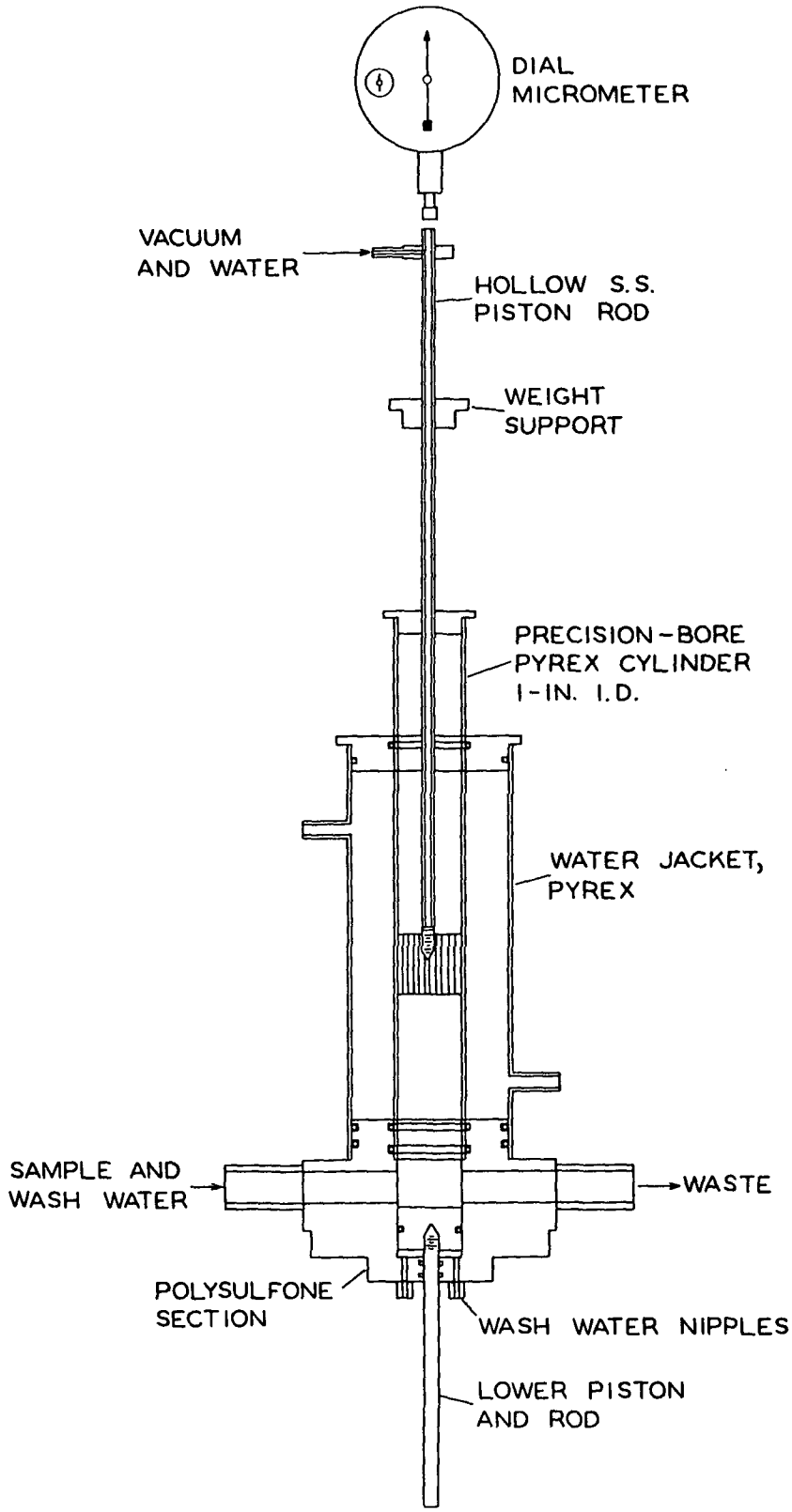


Figure 21. Cross Section of High-Temperature Compressibility Assembly

The cylinder and water jacket are fitted together by O-ring seals into the lower polysulfone assembly and also at the top with a polysulfone cap.

The upper piston is of polysulfone faced with 80-mesh Type 304 S.S. screen fastened to the piston face with a glue made by dissolving polysulfone in methylene chloride. The piston rod is hollow down to the upper face of the piston where two diametrically opposed holes are drilled through the hollow rod wall to permit withdrawal and introduction of liquids from and to the cylinder.

The lower piston, unlike the upper one, is not porous, but is made of solid polysulfone and has a Viton O-ring to seal it against the walls of the glass cylinder when it is in the raised position. The piston rod is of stainless steel, Type 304. When in the lower position, it rests in a close-fitting cavity in the lower polysulfone assembly so that its upper surface forms a tangent with the lower part of the sample and wash line. When the piston is in the raised position, this cavity can also be flushed with water through the two wash nipples indicated in Fig. 21. The entry of the piston rod into the polysulfone assembly is sealed by two Viton O-rings.

The lower polysulfone assembly, into which the pyrex cylinder fits, is machined from a solid block of the plastic. The wash and sample entry nipples are also machined from polysulfone and glued into the block with polysulfone solution in methylene chloride.

Although the compressibility assembly shown in Fig. 21 was not designed primarily as a manually-operated laboratory device but as a possible component of an automatic instrument, initial testing was necessarily by manual operation. This required the use of satellite components not necessarily found in a final instrument. Accordingly, the apparatus was mounted on a solid brass stand and fitted with a dial micrometer for pad thickness measurements.

The sequence of operations for manual testing was as follows:

The bottom piston was raised to enter the pyrex cylinder at a fixed and repeatable height.

A measured volume of pulp slurry at about 0.1% consistency was poured into the top of the cylinder. (The cylinder capacity is about 80 cc.)

The upper piston (weighted) was inserted into the cylinder, lowered slowly into the slurry until a pad formed which supported the piston.

A timer was started and the foot of the dial micrometer placed atop the upper piston rod.

After three minutes' compression time, the micrometer was read, the liquid above the upper cylinder was withdrawn, and both cylinders were lowered so that the pad could be flushed with water out of the apparatus through the waste line.

To calibrate the device for the pad thickness-pad weight relationship, pads were caught in a beaker as they emerged from the waste line, filtered off, dried and weighed. An unbleached kraft pulp made from 100% Douglas-fir (hereafter called kraft pulp no. 1) and having a Kappa number of 54 was used to establish this relationship at two different temperatures, and the results are shown in Fig. 22. The compressing pressure was 41,500 dynes/cm.^{2}.

Since the regression equations for the 23°C. data and the 85°C. data were not much removed with regard to slope and intercept, there appears to be no significant difference in the compression response of this pulp as a result of wide temperature change. This is illustrated in Fig. 22 where the two sets of data are plotted and their common regression line is drawn.

Two additional unbleached kraft pulps were used to establish the pad weight-thickness relationship at 85°C. One was made from a mixture of

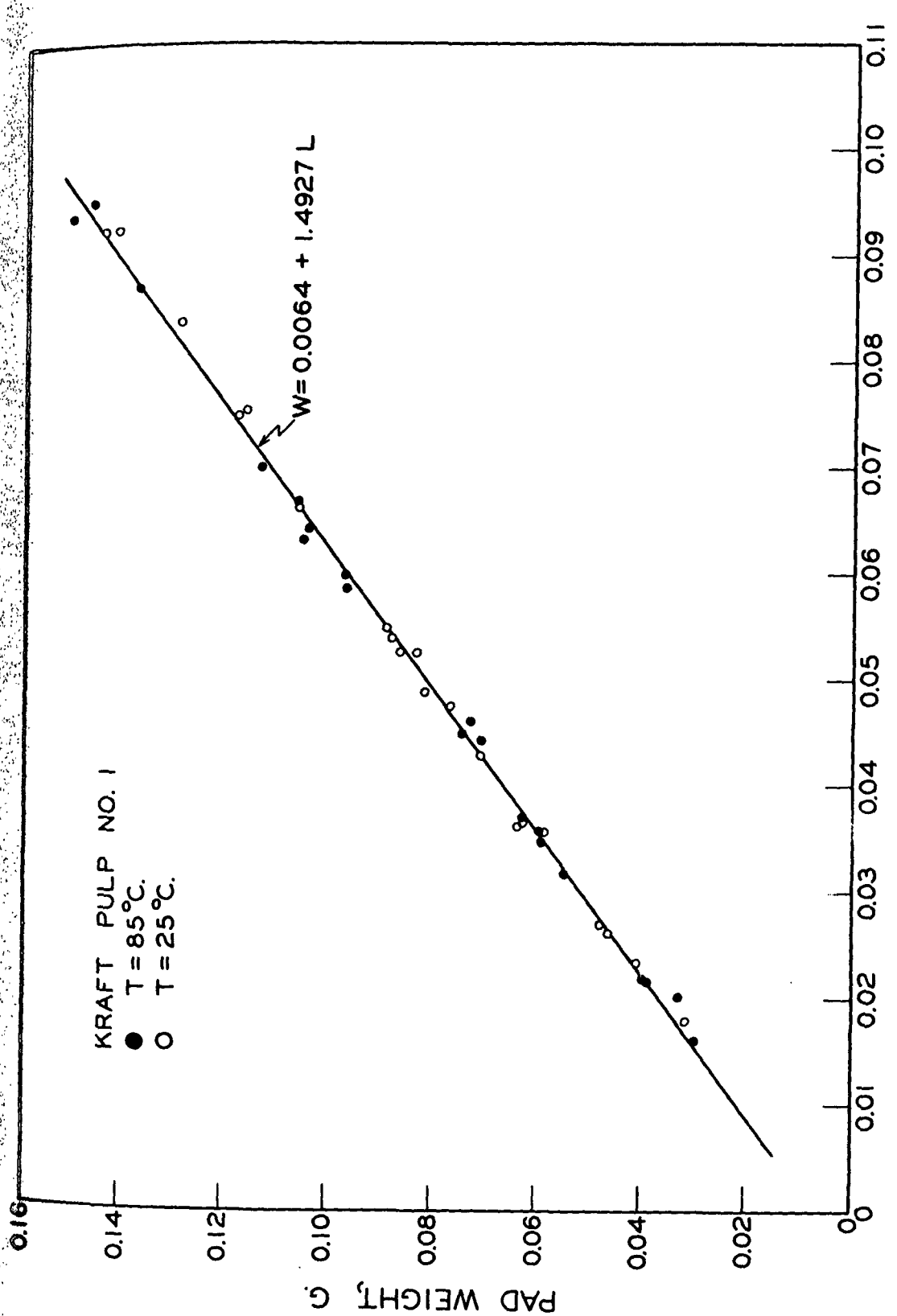


Figure 22. Pad Weight vs. Pad Thickness for Kraft Pulp No. 1 at Two Temperatures

pinewoods that was about two thirds loblolly pine with the rest slash and longleaf pine. This pulp is referred to as kraft Pulp no. 2, and has a Kappa number of 28.5. Kraft Pulp no. 3 was made from southern pine and has a Kappa number of 96.7.

The results for all three pulps at 85°C. are shown in Fig. 23, where their common regression line is drawn through the data points. The relative standard error is 2.62%.

These experiments and the data illustrated in Fig. 22 and 23 show that temperature variations of as much as 60°C. have little effect on the relationship between pad weight and pad thickness. These experiments show further that with suitably designed apparatus such as shown in Fig. 21, very small amounts of pulp can be measured. Additionally, it is shown that the procedure and apparatus are suited for this purpose to pulps of greatly different character.

AUTOMATED DEVICE

Description

The previous experiments, conducted with the two different experimental devices shown in Fig. 17 and 21, respectively, have demonstrated that over a wide range of conditions related to sample size, temperature, sample character, pad diameter, and compressing pressure, the amount of dry fiber in a water-saturated, compressed pad of compressible, fibrous material is a simple linear function of the pad thickness at a fixed compressing pressure. It is, of course, obvious from the mathematical relationships shown in Equations (8)-(10) that at fixed pad thickness the dry fiber content of the pad is also a similar function of the compressing pressure. However, consideration of certain operational characteristics of possible mechanical components has led to the choice of pad thickness as the main measured dependent variable in the device finally designed for automatic operation.

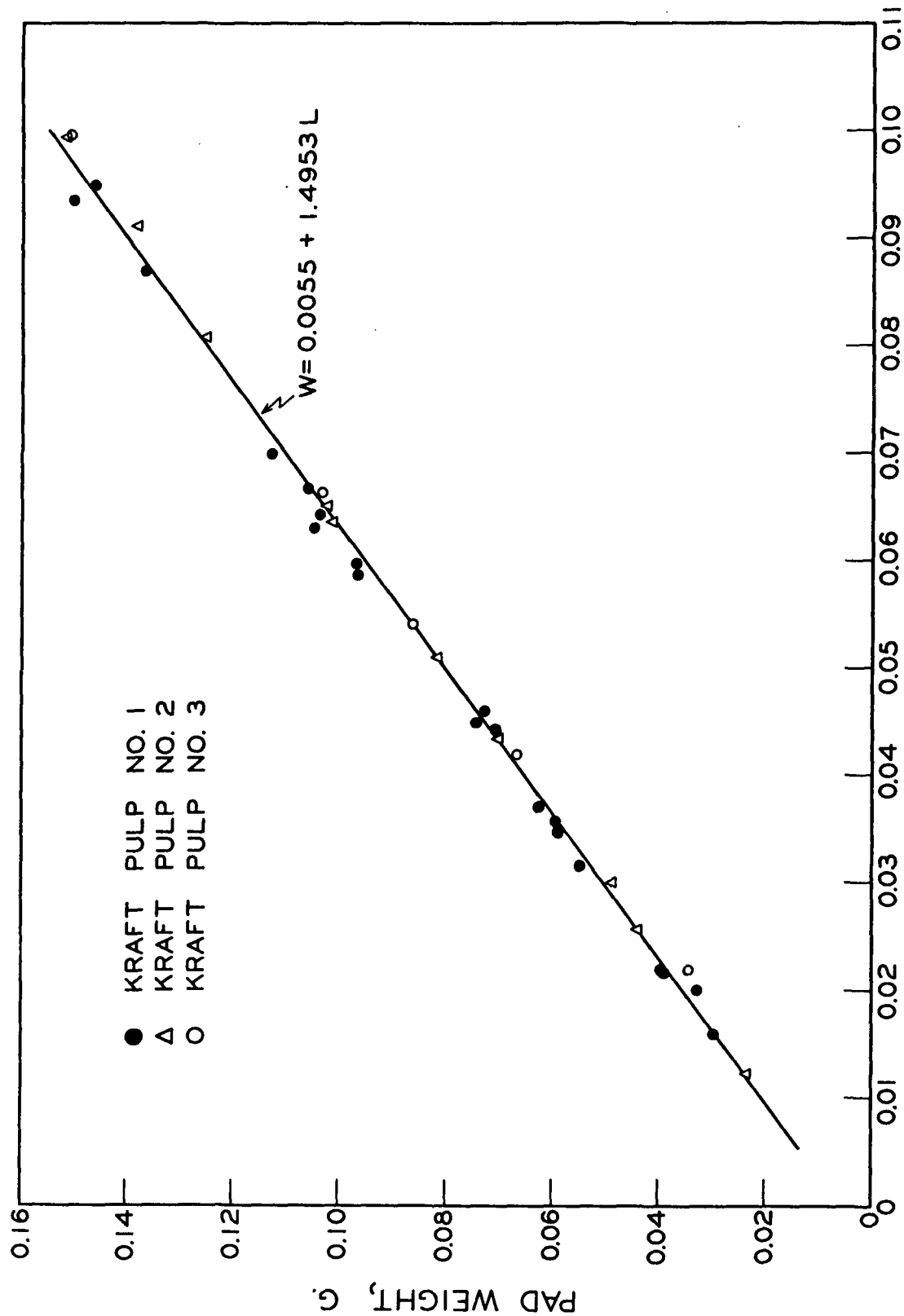


Figure 23. Pad Weight vs. Pad Thickness at 85°C. for Three Different Kraft Pulps

The major component, hereafter called the compressibility component, is shown in detail in Fig. 24. Figure 25 is a simplified block diagram of the overall instrument showing the compressibility component with its associated control and readout components.

The assembly shown in Fig. 24 is essentially similar to that shown in Fig. 21, and consists of a pyrex tube or cylinder fitted with upper and lower pistons and enclosed in a water jacket. Provisions are made for circulating constant-temperature water from a reservoir through the jacket. The construction and purpose of the two pistons are quite different.

The bottom piston is a solid plug of polysulfone plastic connected to a solid stainless steel rod and having a Viton O-ring embedded in its periphery to provide a liquid-tight seal between it and the inner wall of the tube in which it moves. Its function is to provide a solid base or reference point from which to measure the distance between it and the face of the upper piston, and to support the pad, and to contain the slurry in the pyrex tube.

The upper piston consists of a plug of polysulfone plastic through which holes have been drilled to make it porous and which is faced with a disk of 80-mesh stainless-steel woven screen. The other face of the piston is attached to a hollow rod that has two holes drilled through its wall at diametrically opposed positions just above its point of entry into the piston. The opposite end of the piston rod terminates in and is attached to an assembly that holds a fixed weight, is used for moving the piston by virtue of the lift chains, and is connected to the plunger of an LVDT-type linear displacement transducer. A tee-connector at right angle to the upper piston rod provides for connection to services such as water, air, vacuum, etc.

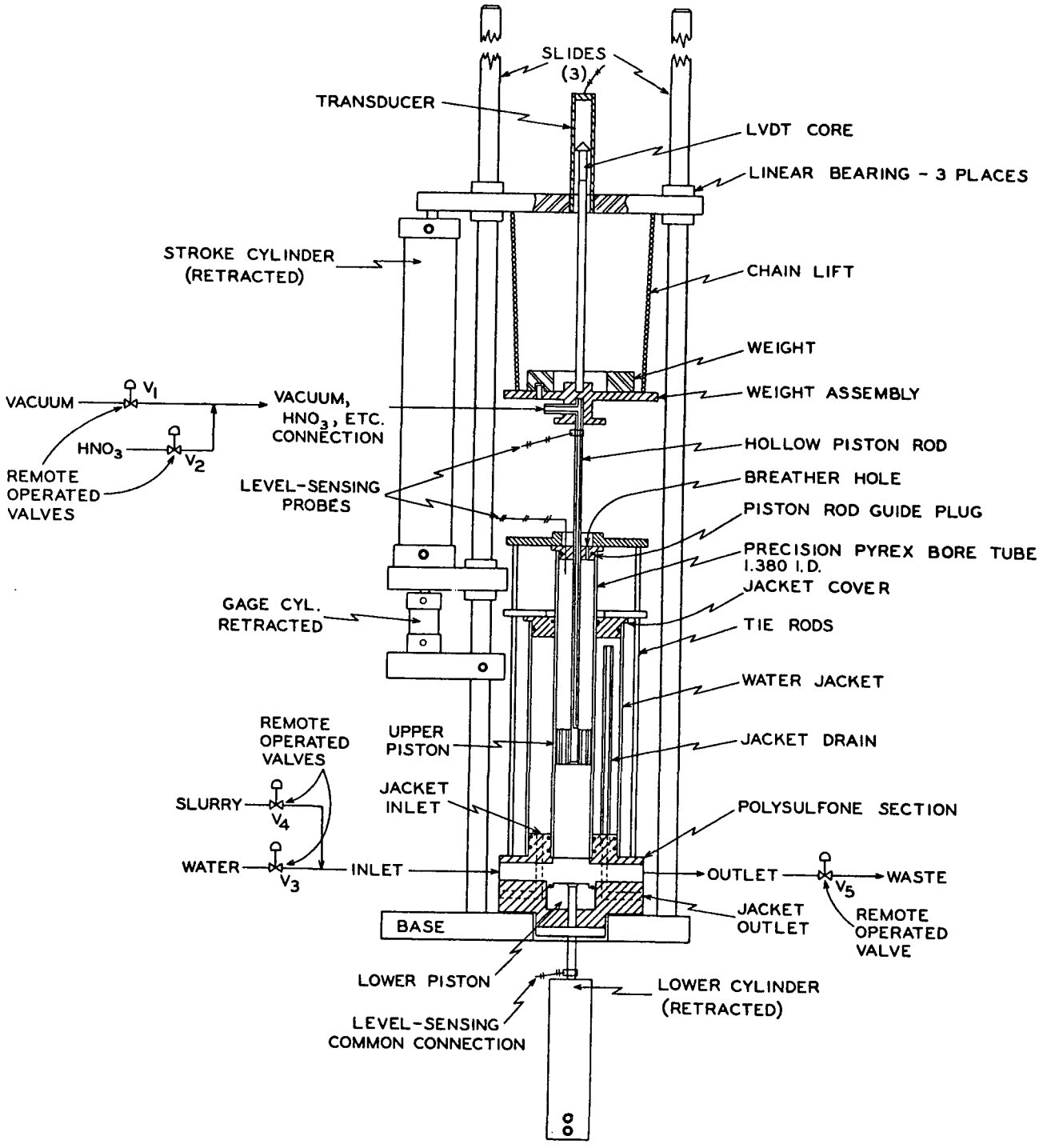


Figure 24. Compressibility Component

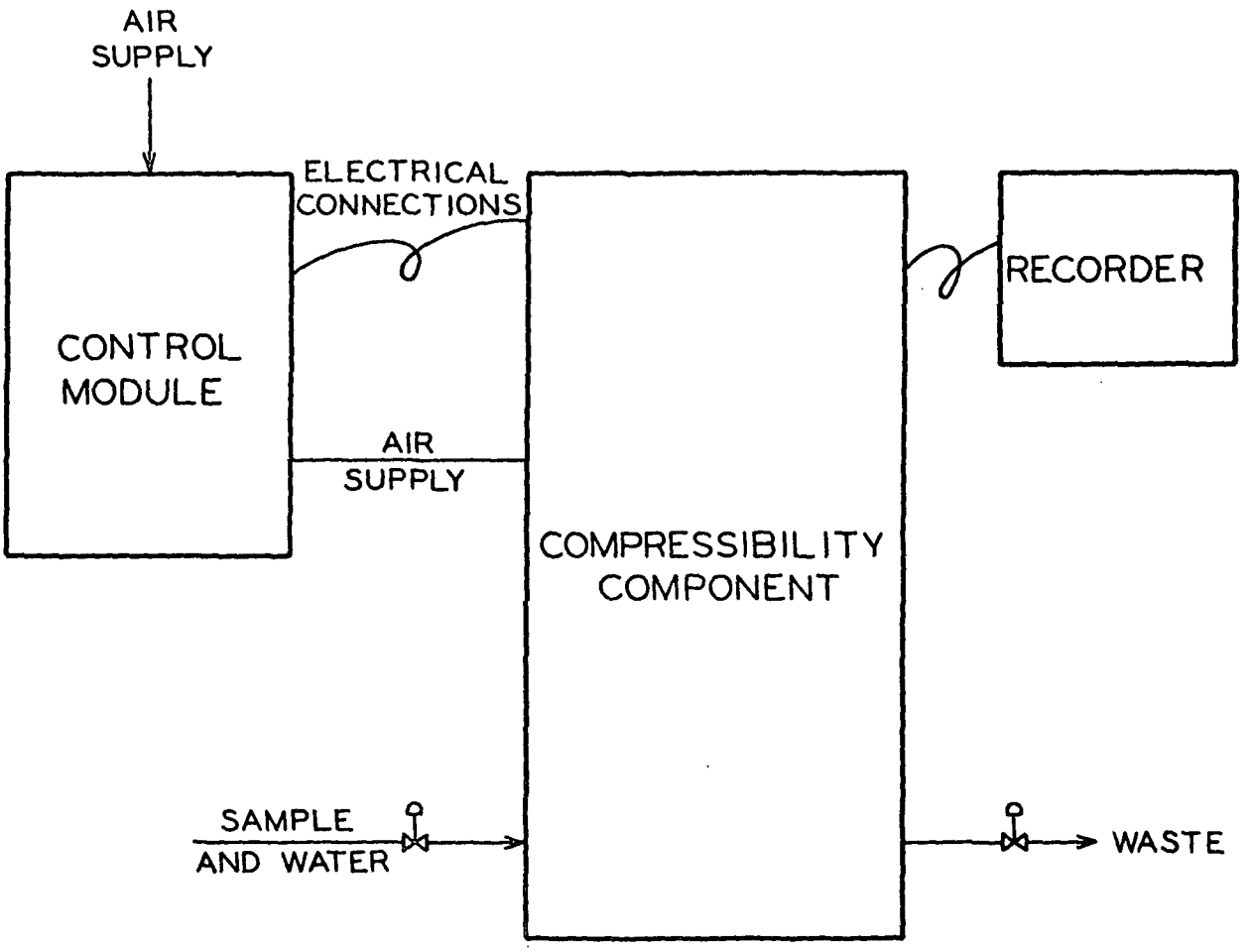


Figure 25. Block Diagram of Instrument for Measuring Dry Fiber Content of Fiber Slurries

The bottom of the pyrex tube is held by O-ring seals in a machined block of polysulfone plastic that has a hole drilled through it at right angle to the axis of the pyrex tube in order to provide for sample and water inlet and for waste outlet.

The system of guides, transducer, lift chains, and cylinders (air operated) are incorporated to allow operation of the device according to a preprogrammed sequence, as described below.

Operation

The control module contains a stepping-drum programmer with appropriate timers, relays, counters, and electrical and pneumatic switches. Appropriate pneumatic and electrical connections exist between the control module and the compressibility component, and between the recorder, control module, and compressibility component. The sequence of operations is as follows:

1. With the lower piston in the retracted position as shown in Fig. 8, the upper piston raised to within about 1/64 of an inch of the level-sensing probe, outlet valve V_5 closed, water valves V_2 and V_3 closed and vacuum valve V_1 closed, slurry valve V_4 is opened to allow fiber slurry from a constant-head reservoir to flow into the apparatus through the inlet and up into the pyrex tube.

2. When the water level reaches the level-sensing probe, an electrical signal causes slurry valve V_4 to close.

3. The stroke cylinder returns to its retracted position at such a rate that the upper piston is prevented from falling freely.

4. When the stroke cylinder is in its retracted position, the upper piston is resting freely upon a pad of fibers strained from the slurry by the downward

movement of the piston and is supported by the lower piston. Also, when the stroke cylinder reaches its retracted position, an electrical signal actuates a time-delay relay.

5. At the end of its time-delay period, the relay closes the circuit between the transducer output and the recorder input and simultaneously actuates another time-delay relay set for about 5 seconds.

6. During the 5-second time period, the recorder responds to the transducer d.c. voltage output to record the signal level. This signal level is proportional to the distance between the faces of the upper and lower pistons, thus measuring the thickness of the pad. The thickness is, of course, proportional to the dry fiber content of the pad through an empirical equation similar to Equations (13) and (14).

7. At the end of the 5-second time period, the transducer-recorder circuit is broken and the recorder pen returns to zero.

8. Upon breaking of the transducer-recorder circuit, outlet valve V_5 is opened, the lower cylinder retracts to place the lower piston below the inlet-outlet in the polysulfone section, the upper piston falls to a position fixed by "stops" so that its face is tangential to the upper surface of the inlet-outlet line, and water valve V_3 is opened. This procedure displaces the pad and water from the glass tube and flushes the system to a waste line. During the flushing period, the vacuum valve V_1 is periodically opened to withdraw liquid and any suspended fibers from above the upper piston.

9. Upon completion of the flushing period, water valve V_3 is closed, outlet valve V_5 is closed, the stroke cylinder raises the upper piston to its position just below the level-sensing probe, and the sequence of operations is repeated.

EXPERIMENTAL RESULTS

The system shown in Fig. 25, incorporating the component shown in Fig. 24, was tested for its ability to automatically measure o.d. fiber content of slurries. A stream of unbleached Douglas-fir kraft pulp at 0.2% consistency was recirculated from a reservoir past slurry valve V_4, and the control module was activated to automatically control the sequence of events.

The LVDT output was read from a voltmeter. The LVDT output covered a range of 0-10 volts d.c., corresponding to a displacement or pad thickness range of 0.0-0.200 inch. The volume of slurry allowed to flow into the compression chamber was varied so as to cover approximately the whole range of the LVDT displacement. The process was repeated at several different levels of temperature in the compressibility component.

To obtain the o.d. pad weight corresponding to each thickness measurement, the fibers forming the pad were caught in a 2-liter beaker during the flushing period, Step 8. The fibers were then filtered on a tared fiberglass filter, dried, and weighed.

The results for the tests conducted at 20 and 85°C. are shown in Fig. 26 and 27, respectively. In Fig. 28 the results of the tests at 85°C. are combined with those at 20, 40, and 60°C. to show that the temperature of the slurry or pad has no discernible effect on the relationship between pad weight and pad thickness, or LVDT output. These results show, further, that the accuracy with which pad weights can be measured in the completely automated apparatus are about the same as in the earlier, manually operated device, the results for which are summarized in Fig. 23.

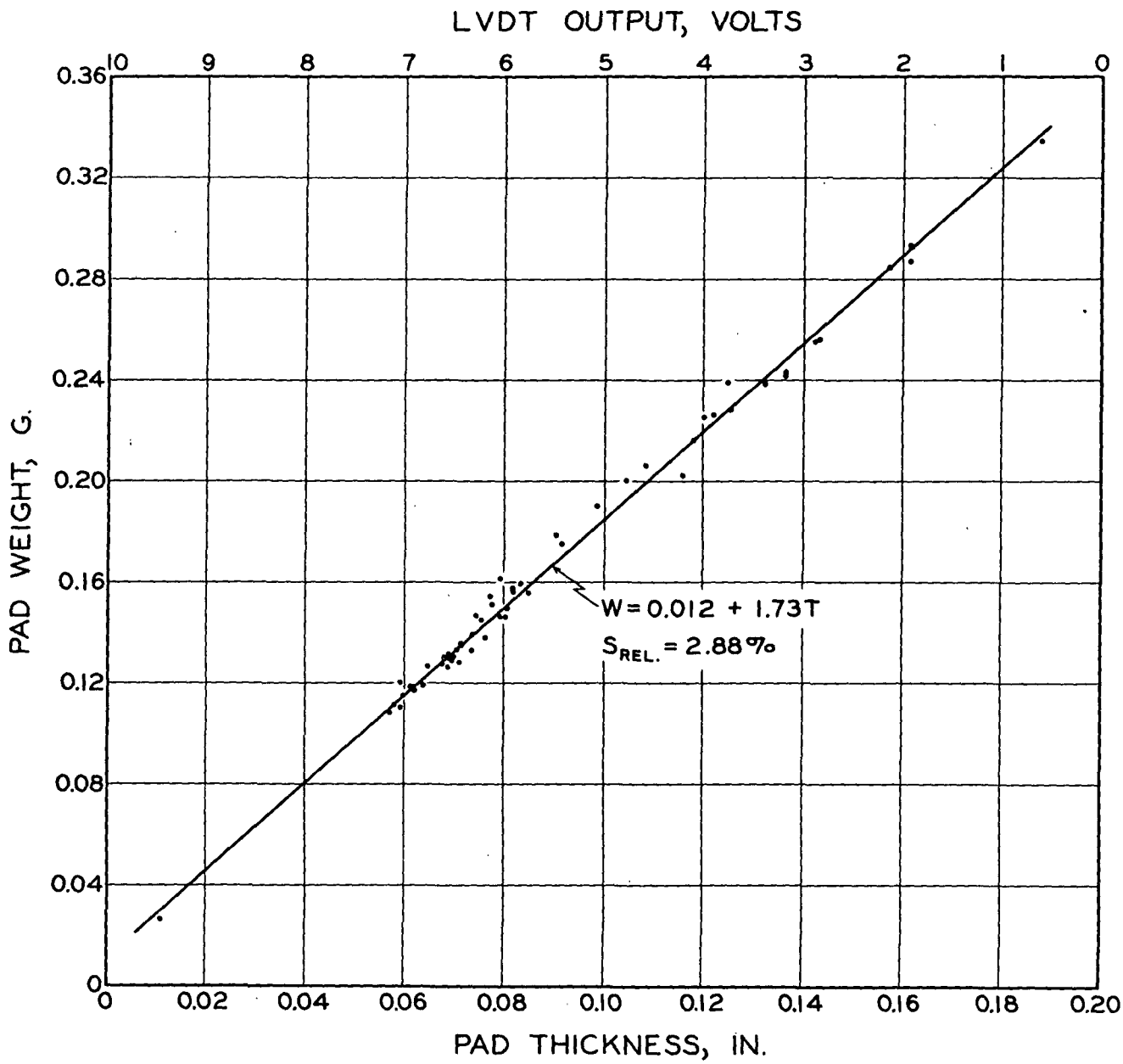


Figure 26. Pad Thickness vs. Pad Weight at 20°C.

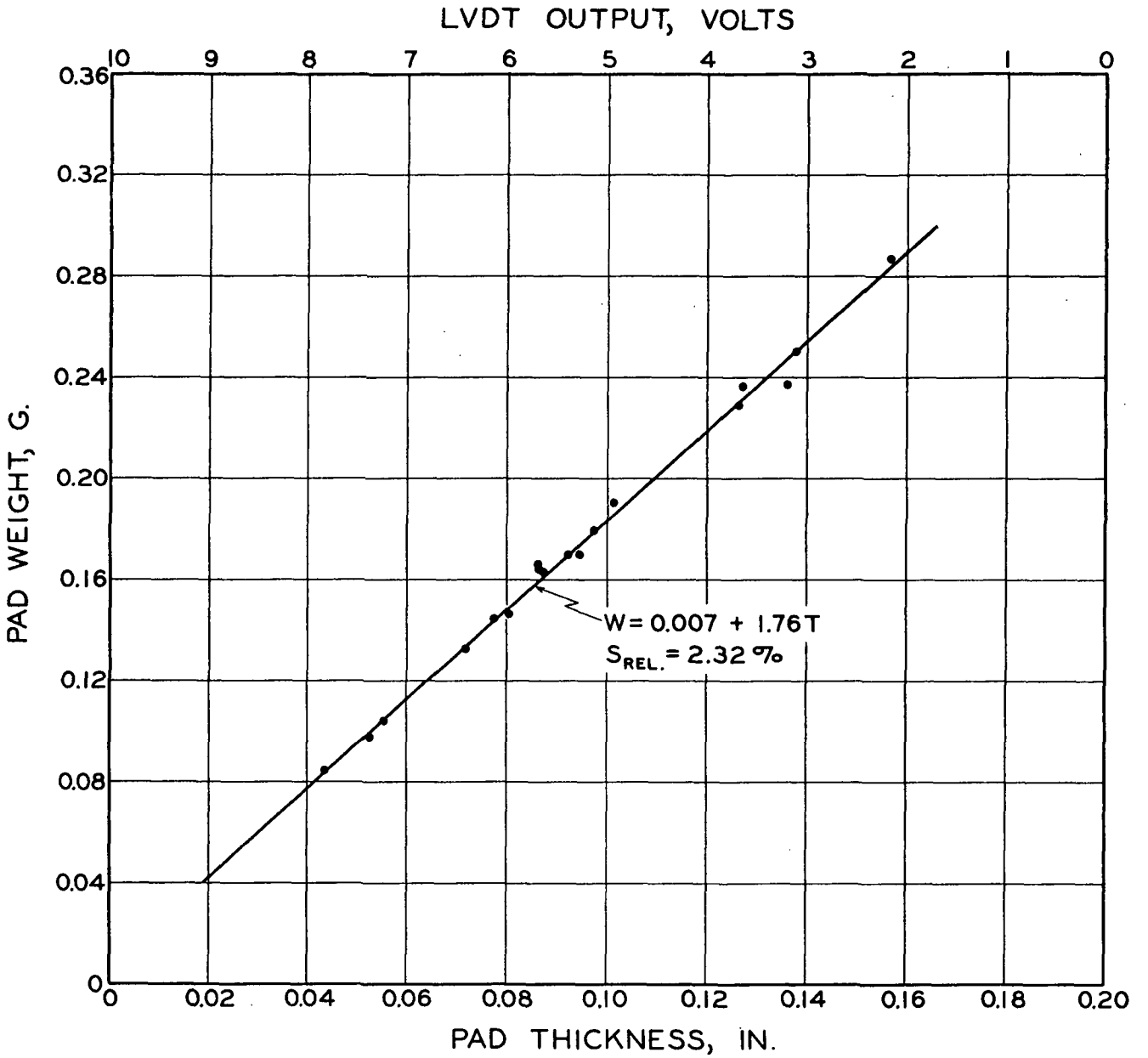


Figure 27. Pad Weight vs. Pad Thickness at 85°C.

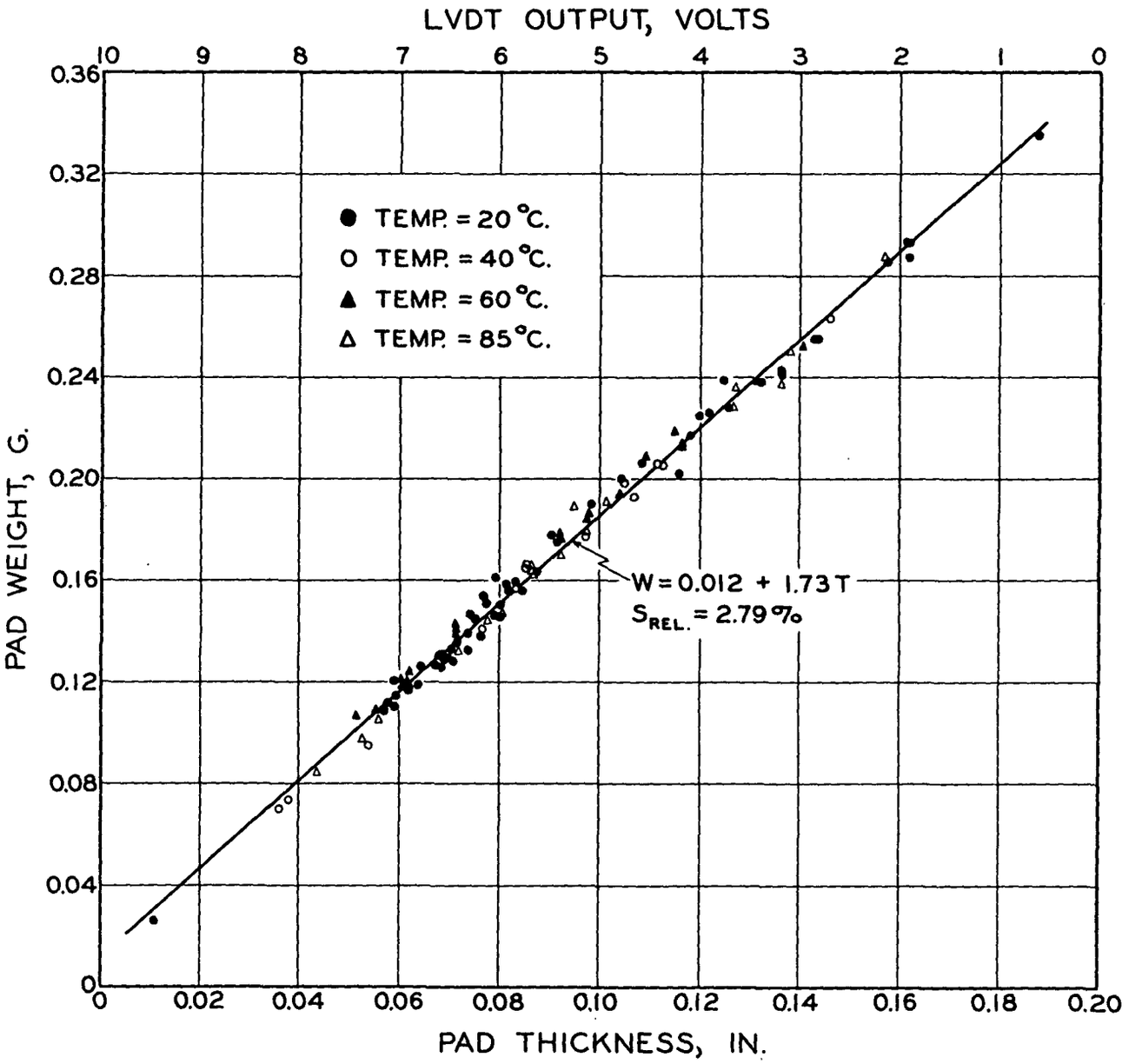


Figure 28. Pad Weight vs. Pad Thickness, All Temperatures

Because of the nature of the mechanical operations that occur during intake of the sample of slurry, a certain amount of variability is encountered in the volume of slurry obtained. To determine the extent of this variability and the resulting variation in pad, or sample, weight, a number of repetitive runs were made with the level sensor in the compressibility component at a fixed setting. The temperature was 85°C. The results are shown in Table XVI.

TABLE XVI

REPETITIVE SAMPLING RUNS AT 85°C.

Run No.	LVDT Output, v.	Pad Thickness, in.	Pad Weight, g.
1	6.15	0.0770	0.1472
2	6.62	0.0676	0.1268
3	7.12	0.0576	0.1150
4	7.10	0.0580	0.1125
5	5.97	0.0806	0.1519
6	6.04	0.0792	0.1458
7	6.32	0.0736	0.1410
8	5.93	0.0814	0.1566
9	6.57	0.0686	0.1294
10	6.48	0.0704	0.1340
11	6.59	0.0682	0.1276
12	6.86	0.0628	0.1238
13	6.52	0.0696	0.1279
14	6.48	0.0704	0.1289
15	6.26	0.0748	0.1449
16	6.93	0.0614	0.1154
Mean			0.1330
Relative standard deviation, %			9.8

Previous work (Progress Report One, p. 64) has shown that when pulp is reacted with a fixed volume of nitric acid, the weight of the pulp may vary ± 16-17% with little effect on the Nu-Number, as long as the actual weight is known. The

data in Table XVI show that weight variations in the automated device are well within these tolerances.

The time-delay relay, mentioned in Step 4 of the sequence of operations of the compressibility component, is continuously adjustable from 0 to 10 minutes. To determine the effect of compression time upon the pad thickness-pad weight relationship, ten runs were made at each of four different compression times. The results are shown in Fig. 29. It is quite evident that in the range covered, compression times as short as two minutes still exceed the time required to reach the "equilibrium" compression rate mentioned earlier.

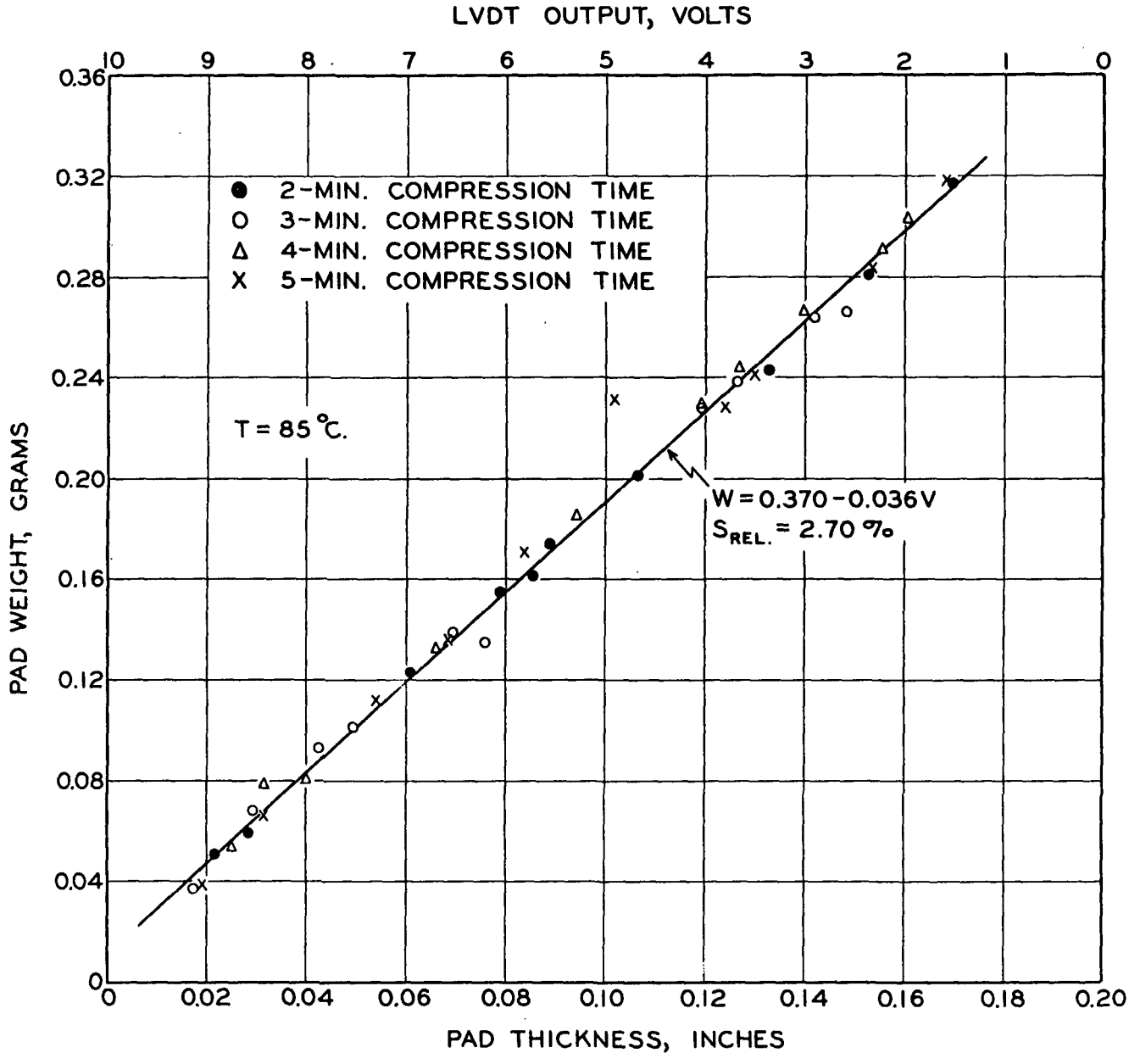


Figure 29. Effect of Compression Time on Weight-Thickness Relationship of Pulp Pads

AUTOMATED MEASUREMENT OF NU-NUMBER

Based upon the "compressibility" method of quantitative sample measurement and upon the nitric acid method of measuring lignin in the sample, an automated device has been assembled and tested in the laboratory. This device was demonstrated at the Project 2634 meeting held March 25, 1969, at The Institute of Paper Chemistry.

The system is essentially that described in the preceding section of this report, the compressibility component of which is shown in Fig. 24. This component is also the reaction chamber for the pulp-HNO_3 reaction. With the addition of several steps to the programmed sequence of operations, previously described, plus a colorimeter to measure the light absorbance of the HNO_3 after reaction with the pulp, the system has the capability of automatically measuring Nu-Numbers.

The colorimeter, which was of special design for this application, has an output of 0-10 volts d.c., corresponding to an absorbance range of 0-0.5. This d.c. voltage output can be fed to a recorder, a panel meter, an analog computer, or to an analog-to-digital converter at the option of the user.

The LVDT output is also 0-10 volts d.c., corresponding to a pad weight (or thickness) range of 0-0.4 g. Thus, the two outputs, colorimeter and LVDT, are used to compute the Nu-Number according to the general formula:

$$Nu = \frac{A \times B \times X}{C \times Y} \qquad (15)$$

where:

$\underline{A}$ = mg./liter of $K_2Cr_2O_7$ standard,

$\underline{B}$ = milligrams desired pad weight,

$\underline{C}$ = absorbance of $K_2Cr_2O_7$ standard,

$\underline{X}$ = absorbance of reacted HNO_3, and

$\underline{Y}$ = milligrams actual pad weight.

In actual operation, $\underline{A}$, $\underline{B}$, and $\underline{C}$ will be constant, having values of 100, 100, and 0.16, respectively. $\underline{X}$ is derived from the regression equation relating colorimeter output voltage to absorbance, and $\underline{Y}$ is derived from the regression equation relating LVDT output voltage to pad weight. Both regression equations are empirically established by calibration.

Four different unbleached softwood kraft pulps derived from different softwood species were used in experiments to establish the operating characteristics of the system. In completely automatic operation, the system was allowed to make ten repetitive measurements on each of the four pulps with a desired pad weight of 100 mg. The LVDT and colorimeter outputs were visually recorded from panel voltmeters and the Nu-Number was computed from these readings. The results are shown in Table XVII.

The mean Nu-Numbers of the four pulps are plotted against the corresponding Kappa numbers in Fig. 30, where it is seen that the relationship is linear. Inspection of Table XVII shows that the variance in the Nu-Numbers is an apparent function of the precision with which the absorbance of the reacted HNO_3 is measured. For example, the absorbance values for Pulp no. 4 are all 0.013 or lower, and a variance of 0.001 will result in a 7.7% error from this cause alone. However, this source of error in future measurements of the Nu-Number of low-lignin pulps can be circumvented by using less HNO_3, by using more pulp, or both. The result would be an increase in the absorbance of the reacted HNO_3 with corresponding increase in the relative precision of measurement.

TABLE XVII

AUTOMATIC NU-NUMBERS

Reaction temperature = 85°C.; reaction time = 12 minutes.

Pad Wt., mg.	Absorbance	Nu-Number	Pad Wt., mg.	Absorbance	Nu-Number
Pulp No. 1 (Kappa no. = 54.0)			Pulp No. 2 (Kappa no. = 32.0)		
116	0.099	54.0	86	0.035	25.7
103	0.088	54.0	84	0.034	25.6
95	0.079	52.7	90	0.038	26.8
99	0.082	52.4	76	0.027	22.5
112	0.097	54.8	75	0.027	22.8
100	0.087	55.0	78	0.029	23.6
102	0.088	54.7	80	0.029	22.9
108	0.084	49.2	74	0.026	22.2
96	0.080	52.8	75	0.027	22.8
98	0.081	52.4	74	0.026	22.2
Rel. standard deviation (Nu) = 3.1%.			Rel. standard deviation (Nu) = 6.7%.		
Pulp No. 3 (Kappa no. = 23.2)			Pulp No. 4 (Kappa no. = 15.4)		
112	0.034	19.2	115	0.013	7.1
108	0.031	18.1	114	0.012	6.7
108	0.030	17.6	106	0.009	5.4
107	0.029	17.1	102	0.013	8.1
105	0.029	17.5	103	0.011	6.8
105	0.029	17.5	114	0.011	6.1
113	0.029	16.2	118	0.012	6.4
112	0.031	17.5	106	0.009	5.4
114	0.030	16.7	110	0.013	7.5
114	0.032	17.8	105	0.012	7.2
Rel. standard deviation (Nu) = 4.36%.			Rel. standard deviation (Nu) = 12.5%.		

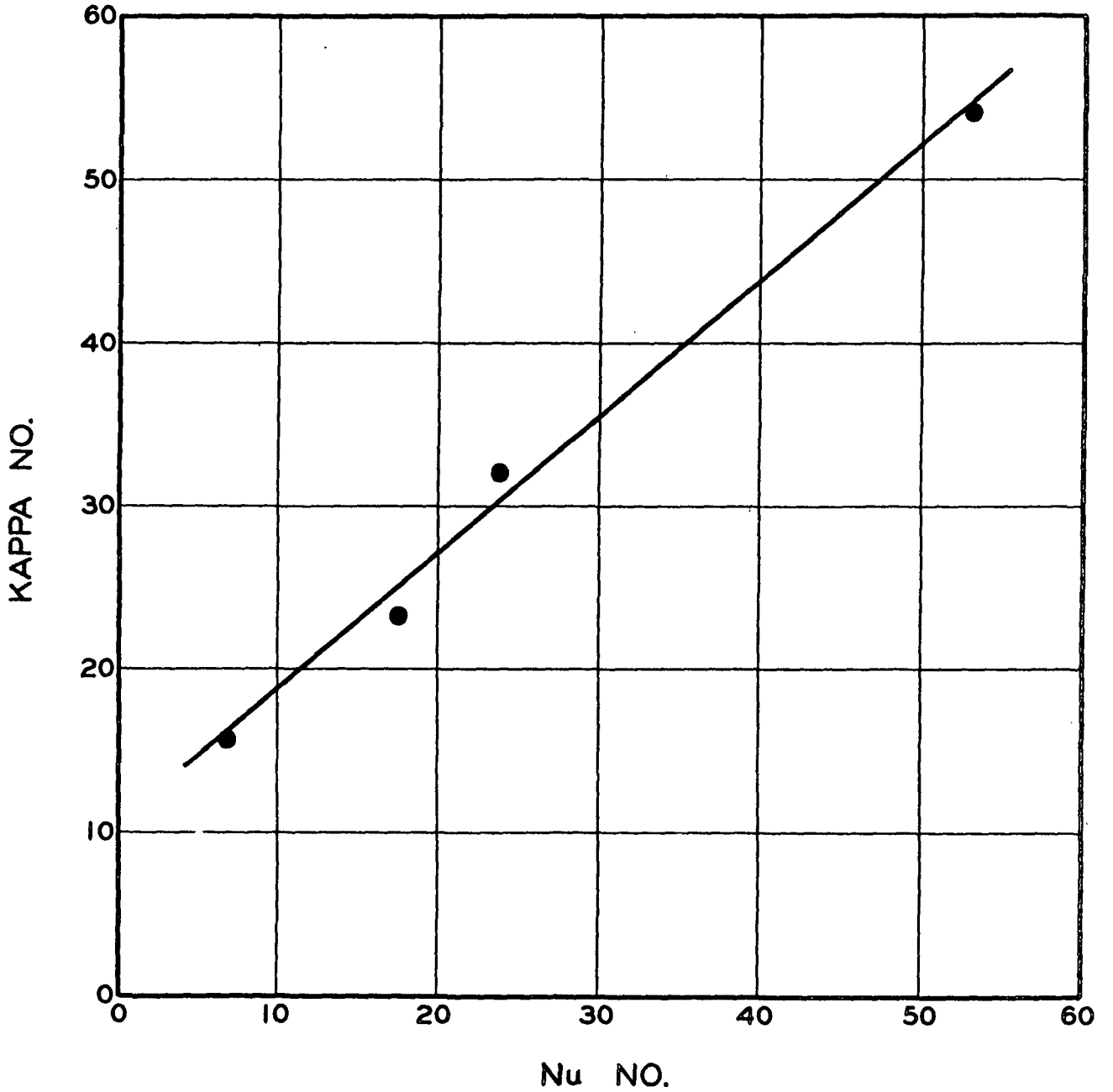


Figure 30. Mean Nu-Number Values vs. Kappa Number

FUTURE WORK

The automated device for measuring residual lignin in pulp, called the Nu-Number Monitor, has been sufficiently tested in the laboratory to establish that it does, in fact, have the capability of measuring residual lignin with a precision that appears comparable to that obtained from manual permanganate number tests. The total cycle in completely automatic mode is 17 minutes; that is, 17 minutes elapse from the moment the slurry sample enters the instrument until the test result is obtained.

INDUSTRIAL SAMPLING

To obtain a primary sample of stock and to prepare it in a manner acceptable to the instrument, a sampling system has been designed in cooperation with Krofta Engineering Corporation of Lenox, Massachusetts. This particular design is applicable to stock that has been screened. It is shown in Fig. 31.

The following requirements and specifications apply to the sampler:

1. The sampler should take a constant, preset amount of pulp stock of about 1% consistency from an open vat.

2. Such stock sample should be washed 1-4 times with fresh water and the wash water rejected.

3. The sample should be diluted about tenfold to obtain a consistency of about 0.1%.

4. The volumes of the undiluted sample, as also the volumes of the diluted sample, should be adjustable.

5. The number of washings should be adjustable.

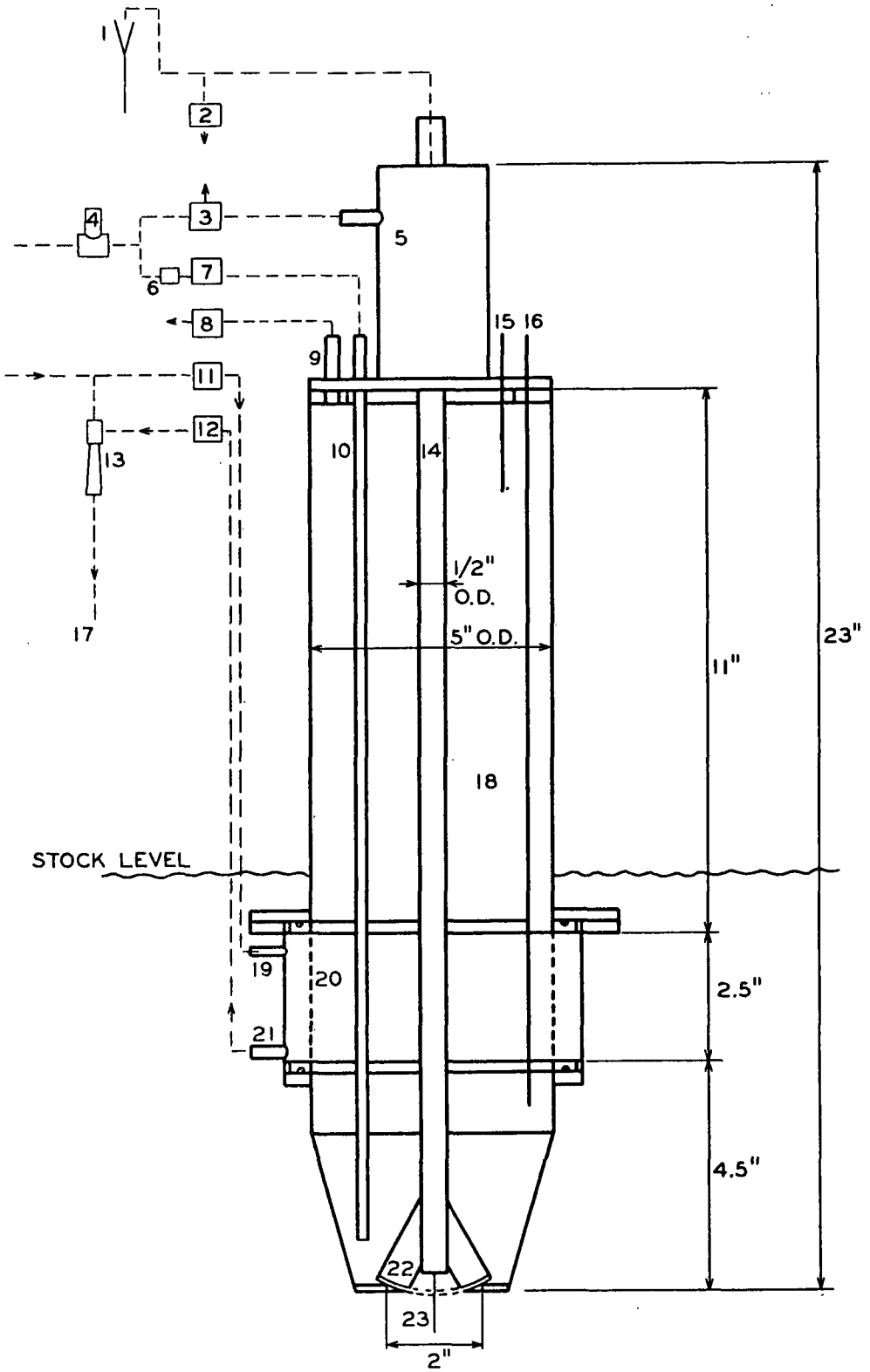


Figure 31. Stock Sampler

6. The sampler should be built with all parts in contact with the stock of 316 stainless steel.

7. Compressed air of about 60 p.s.i., electrical current of 110 volts, 60 cycles, single phase, and fresh water are available.

8. The total cycle for taking, washing, and diluting the sample should not exceed 10 minutes.

Its operation, controlled by an automatic programmer, is as follows:

The sampler is submerged in stock 7 to 10 inches. When the bottom valve opens, stock enters the sampler, and at contact with the bottom electrode (16) the bottom valve (22) closes. In this way, a preset volume of undiluted and unwashed sample is taken into the sampler.

Inside the sampler, over the sample level, a ring is built of perforated plate and enclosed into an outer ring.

Fresh water enters at (19) into the sampler body. When the water and stock level reaches the upper electrode, intake of fresh water is cut off.

Compressed air enters through the bubbling tube (10) at a controlled rate and mixes with the stock and water. After about 25 seconds, drain valve (12) opens and suction is applied behind the perforated plate (20). Such suction is produced with an injector (13) fed by high-pressure water (minimum 30 p.s.i.). The stock collects on the perforated plate (20) and the wash water is discharged. After the level drops to the upper part of the perforated plate, air enters and the drainage stops.

The drain valve closes and fresh water enters the sampler body again until the top electrode is reached. Draining can take place again and the procedure of

diluting and washing can be repeated up to four times. With four washings, the original liquid of the undiluted sample would be reduced to 1/16 of the original concentration.

After the last fresh-water dilution, the sample is mixed for about 30 seconds, the sampler vent closes, and the sample is ejected through the central hollow shaft.

During the ejection of the sample, solenoid valve (2) opens for a short period and takes the sample to the Nu-Number Monitor.

After this, air ejects the sample completely and the cycle stops.

In order to start a new cycle, a short electrical impulse from the Nu-Number Monitor is required to bridge the built-in self-stop in the sampler programmer.

The legend for Fig. 31 is as follows:

1. Overflow and drain of the unused diluted sample.
2. Solenoid valve delivering sample to the Nu-Number Monitor.
3. Three-way solenoid valve for operation of the sampler piston for opening and closing of the bottom 2-inch inlet (23).
4. Pressure-reducing valve with gage for compressed air.
5. Sampler piston body.
6. Needle valve to set the flow of air to the bubbler-mixer tube (10).
7. Solenoid valve delivering air to the bubbler-mixer tube (10).
8. Solenoid valve for venting the sampler.
9. Vent tube.
10. Bubbler-mixer tube for mixing the sample with air.
11. Solenoid valve for dilution of fresh water.

12. Solenoid valve for drain of wash water.

13. Injector.

14. Central hollow stem of the sampler for sample ejection.

15. Upper-level electrode.

16. Lower-level electrode.

17. Discharge of the injector to drain.

18. Sampler body.

19. Inlet for fresh water.

20. Ring made of perforated screen of same perforations as used for Canadian Standard Freeness Tester.

21. Outlet for wash water.

22. Bottom closing ball-form plate.

23. Bottom opening (2-in. diameter) for the inlet of undiluted sample.

This sampler is a design modification of a standard sampler for stock, sewage, liquid industrial effluents, etc., which has been supplied for years by Krofta. It has not, however, been put to use in the manner described above. Part of the future work will be to obtain one of these samplers and integrate its operation with that of the Nu-Number Monitor. This will be done in the laboratory before the whole system is placed in a mill.

ENCLOSURE OF COMPRESSIBILITY COMPONENT

At the present time, the Nu-Number Monitor consists of essentially two modules: (1) the control system, including the programmer and electrical and pneumatic circuitry associated with it, the colorimeter, the various level-sensing devices, etc., and (2) the compressibility component shown in Fig. 24, which is also the reaction chamber for the pulp-HNO_3 reaction.

The control system is housed in a painted steel NEMA 12 cabinet, but the compressibility component stands in the open. Part of the future work will be to enclose this component in a steel housing suitable for a mill environment and to provide for electrical and pneumatic cable connections between it and the control module. This is not a major task, but requires some detailed mechanical design.

INDUSTRIAL TRIAL

Once the compressibility component is suitably enclosed and the stock sampling system has been obtained and laboratory tested, the entire system will be ready for installation in a mill. Although it is anticipated that its application will eventually include blow-line or blow-tank sampling, the initial industrial trial will be made under the simplest conditions possible. It is intended that this be on screened, washed stock where the stock is at perhaps 1-2% consistency. This condition exists in the decker vat.

The site of the mill trial has not been selected, although several have been under consideration for several months. The trial will, of course, be undertaken in a mill of one of the members of this project.

TIME AND BUDGET

It is anticipated that the cost of the work described above will be approximately $60,000 and that the elapsed time from initiation to completion will be 6-8 months. This along with the details of cost sharing amongst the member companies, is described in more detail in Mr. Wendall Smith's letter accompanying this report.

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